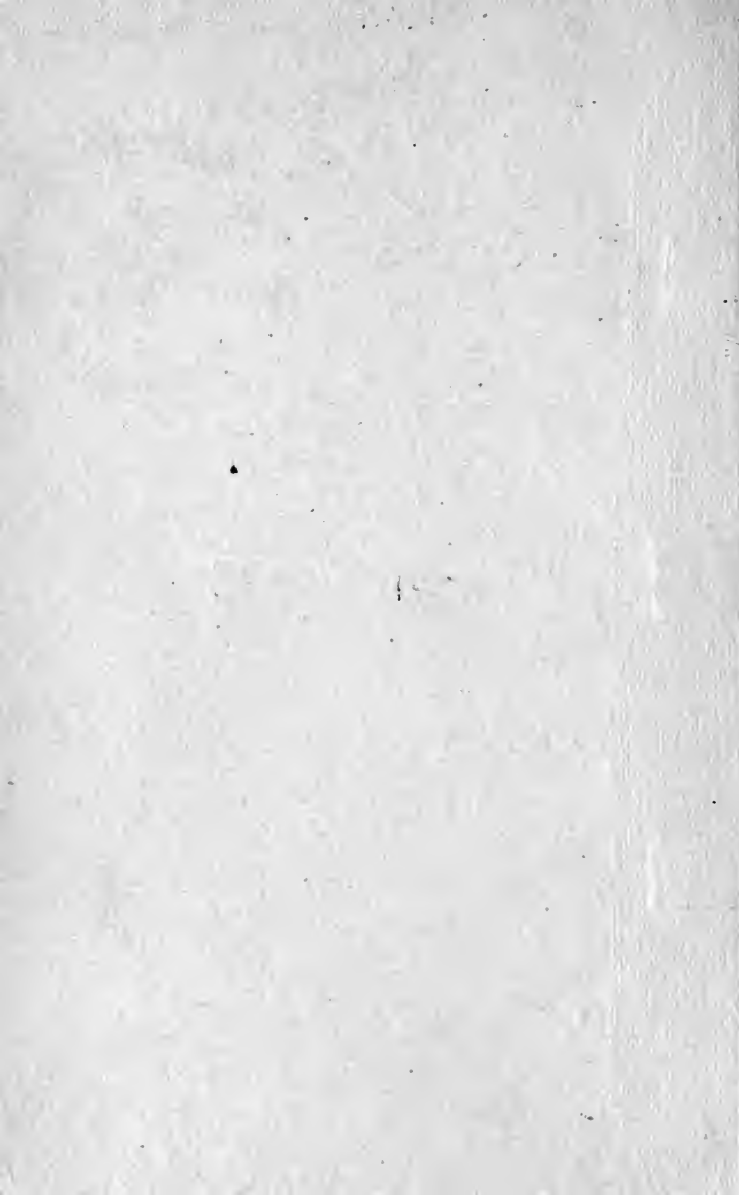




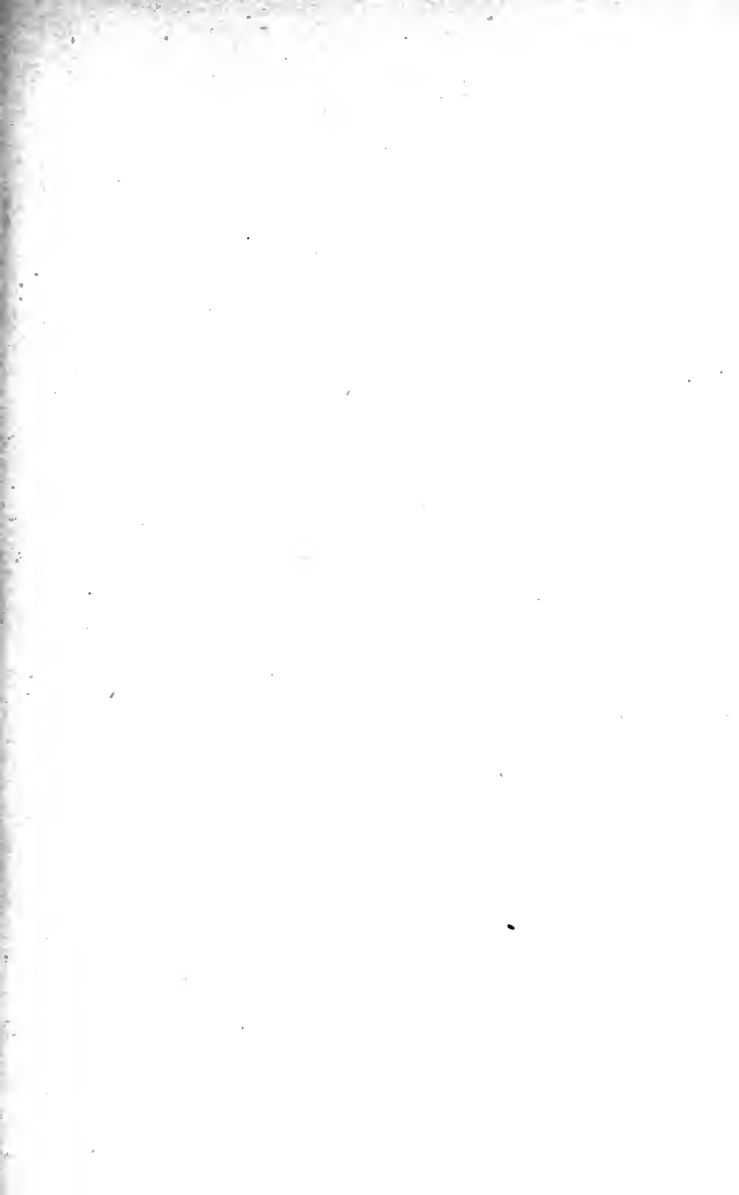
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A COURSE OF QUANTITATIVE ANALYSIS  
FOR STUDENTS



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WITH THE PUBLISHERS  
COMPLIMENTS.

# QUANTITATIVE ANALYSIS

## FOR STUDENTS

BY

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noel</sup>  
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## P R E F A C E

“One may be a good analyst without having tried *every* method, or determined *every* body.”—FRESSENIUS.

It is believed by the author that the following examples will prove as useful elsewhere as in his own laboratory. The methods of analysis employed are such as have been found accurate and useful. They are taken from various sources, such as the invaluable treatise on *Quantitative Analysis* of Fresenius, *Précis d'Analyse Chimique* of Gerhardt and Chancel, Sutton's *Volumetric Analysis*, Lunge and Hurter's *Alkali-Maker's Pocket-Book*, and many other publications.

Some few of the methods and arrangements are original. The examples worked out have, for the most part, been copied from the students' notebooks during the past session. The number of examples might have been increased, but it was not considered judicious to enlarge the work.

All the analytical operations involved are such as can be carried out without the use of complicated apparatus.

To the student it may be remarked, that to be a good analyst does not necessitate a profound knowledge of chemistry, nor does the possession of extensive knowledge and a brilliant intellect enable one to dispense with practice in the execution of analytical operations.

ROYAL COLLEGE OF SCIENCE, DUBLIN,

*6th May 1887.*



# QUANTITATIVE ANALYSIS

## WEIGHTS AND MEASURES OF THE METRICAL SYSTEM

Metre.	Millimetres.	Abbreviations.
1	= 1000	m.m.
	Centimetres.	
	= 100	c.m.
	Decimetres.	
	= 10	d.m.

Cubic Centimetre.	Gram.	Abbreviations.
1	of water at 4° C. weighs 1	gr.

Cubic Centimetre.	Litre.
1000	„ „ measure 1 L.

Grams.	Kilogram.
1000	„ „ weigh 1 kilo.

Gram.	Milligrams.	Abbreviations.
1	= 1000	ml.gr.
	Centigrams.	
	= 100	c.gr.
	Decigrams.	
	= 10	d.gr.

A litre flask when filled, so that the lowest point of the meniscus coincides with the mark on the neck, should hold 998 grams of distilled water weighed with brass weights in air at 15° C., and at normal pressure 760 m.m. The volume of this quantity is equivalent to that of 1 kilo. of water weighed *in vacuo* at 4° C., *i.e.* 1000 c.c.

### ENGLISH EQUIVALENTS.

Metre.		Feet.	Inches.
1	=	3·280899,	about 39

Gram.		Grains.
1	=	15·432

		Pounds
Kilo.		Avoirdupois.
1	=	2·2046

Litre.		Gallon.
1	=	0·2201

Inch.		m.m.
1	=	25·3995

Gallon.		c.c.
1	=	4536

Quart.		c.c.
1	=	1134

Pint.		c.c.
1	=	567

ENGLISH EQUIVALENTS—*Continued.*

Cubic

Inch.

c.c.

$$1 = 16.3862$$

Fluid

Ounce.

c.c.

$$1 = 28.35$$

Pound

Avoirdupois.

Grams.

$$1 = 453.6 \text{ nearly.}$$

Ounce

Avoirdupois.

1

Grams.

$$437\frac{1}{2} \text{ grains} = 28.35$$

Pound

Troy.

Grams.

$$1 = 373.24195$$

Ounce

Troy.

1

Grams.

$$480 \text{ grains} = 31.1035$$

Avoirdupois.

Gallon.

lbs.

oz.

Grains.

$$1 = 10 = 160 = 70,000$$

TABLES GIVING THE DIMENSIONS OF VARIOUS  
PIECES OF APPARATUS.

BEAKER GLASSES.

Diameter across bottom.		Height.		Contents. Cubic centimetres.
Inches.	Millimetres.	Inches.	Millimetres.	
$3\frac{1}{2}$	90	$6\frac{1}{2}$	165	1050
$3\frac{1}{4}$	80	6	150	880
3	76	$5\frac{1}{2}$	137	715
$2\frac{1}{2}$	62	$4\frac{3}{4}$	120	515
$2\frac{1}{4}$	56	$4\frac{1}{8}$	105	365
2	51	$3\frac{3}{4}$	95	260
$1\frac{3}{4}$	45	$3\frac{1}{4}$	89	190
$1\frac{1}{2}$	40	$2\frac{3}{4}$	70	125
$1\frac{3}{8}$	35	$2\frac{1}{2}$	63	85
$1\frac{1}{4}$	30	$2\frac{1}{8}$	55	60

PORCELAIN BASINS.  
(With round bottoms.)

Diameter.		Capacity. Cubic centimetres.
Inches.	Millimetres.	
3	76	50
$3\frac{1}{4}$	84	70
$4\frac{1}{8}$	105	150
$5\frac{3}{4}$	141	200

## PORCELAIN CRUCIBLES.

Greatest diameter.		Height.		Capacity. Cubic centimetres.
Inches.	Millimetres.	Inches.	Millimetres.	
$2\frac{5}{8}$	67	$1\frac{5}{8}$	45	70
$1\frac{3}{4}$	43	$1\frac{1}{8}$	29	17
$1\frac{1}{4}$	33	1	26	10
1	24	$\frac{3}{4}$	19	4

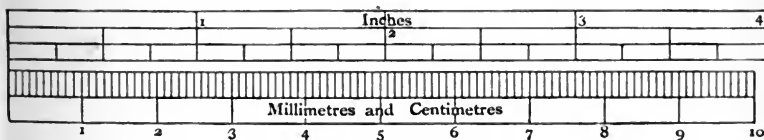
ROSE'S CRUCIBLE for heating Sulphides in a Current of  
Hydrogen or Sulphuretted Hydrogen—

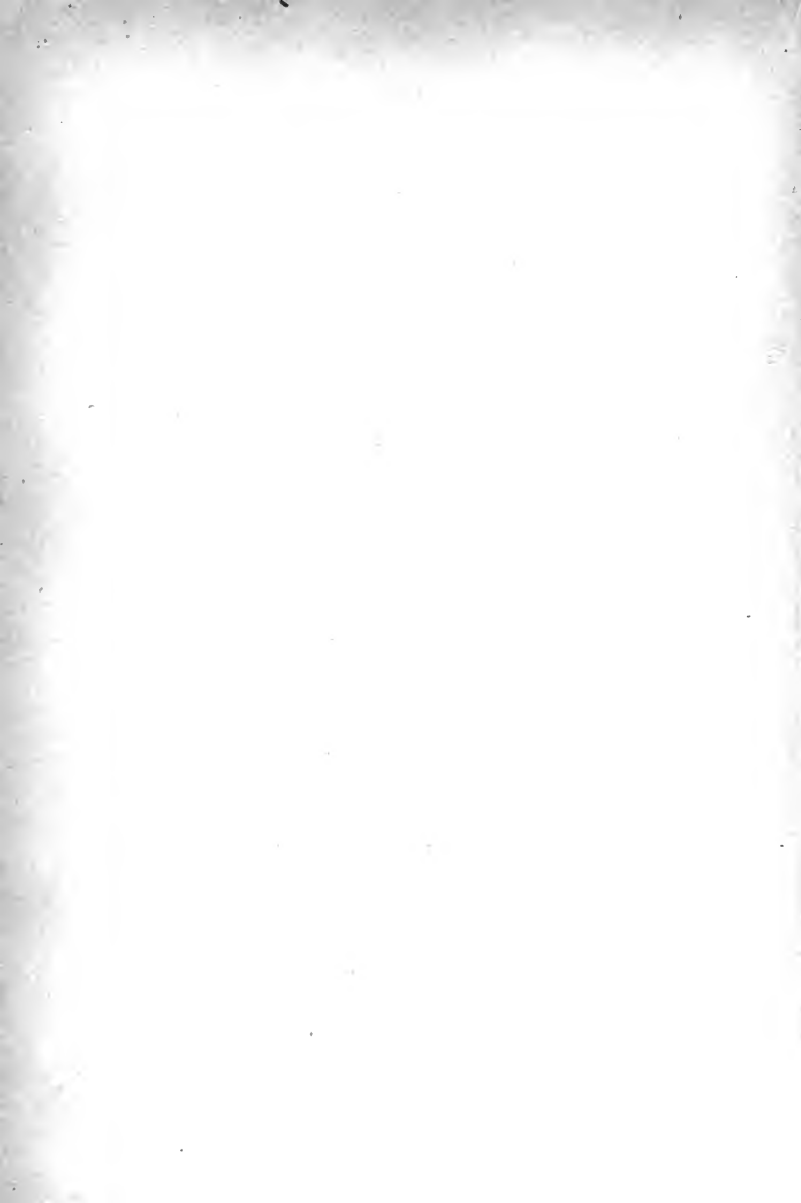
Greatest diameter .  $1\frac{3}{16}$  inches. 28 millimetres.

Height . . .  $1\frac{1}{2}$  „ 39 „

Length of tube . .  $5\frac{3}{8}$  „ 139 „

The tube projects through a hole in the lid  $\frac{3}{4}$  inch within the crucible.





## INTRODUCTION

CHEMICAL analysis is the art of determining the exact composition of substances and stating the proportions of their components in an intelligible form. In most cases it is based upon the separation of the constituents in the condition of definite and unalterable compounds of known composition in a state of perfect purity; ascertaining the weight of the compounds obtained from a given quantity of the material, and calculating the amount of one or more of the elements it contains.

The operations which this process involves are generally the following :—

Selecting or sampling.	Precipitating.
Pulverising.	Decanting and syphoning.
Weighing.	Filtering.
Drying.	Washing.
Dissolving.	Igniting or burning.

No series of operations requires greater nicety in handling, care and patience in execution, attention to details, and closer observation, than such as may be

employed in the analysis of a single mineral. The mechanical and chemical operations are only a part of the process of analysis; the calculation of the results, the deductions therefrom, and the final statement, are details of equal importance. For technical purposes it is frequently unnecessary to determine the quantity of more than one constituent; for instance, all we require to know about bleaching powder is the quantity of chlorine which is available for the purpose of bleaching, and a simple estimation of this may readily be made by the method of volumetric analysis, which will be described later.

Some of the above operations which require particular care may now be described in detail.

**Pulverisation.**—Substances to be analysed should be reduced to powder, for not only are they thus rendered more easily soluble, but an average sample may be taken from a powder which often would be impossible

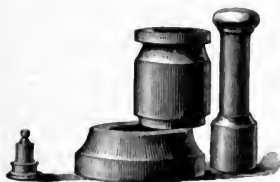


FIG. 1.—Steel Mortars for crushing Minerals.

from a solid. Substances which are not hard may be ground in a porcelain mortar. Hard minerals are crushed to powder in a steel mortar (Fig. 1), which is seen to be composed of three parts

fitting one into the other, the dimensions of which are : outside diameter of base,  $8\frac{3}{4}$  inches ; inside,  $4\frac{1}{2}$  inches ;



height,  $3\frac{1}{8}$  inches ; outside diameter of body, 5 inches ; inside, 3 inches ; height,  $6\frac{1}{2}$  inches ; pestle, total length,  $11\frac{1}{4}$  inches.

The powder obtained from the mineral is turned over and crushed again, so that the coarser particles are reduced as far as possible by crushing. The mineral is sifted, and the finer particles are ground in a mortar made of agate, which may be  $2\frac{1}{2}$  to 5 inches in diameter, until there is no feeling of grittiness when the powder is taken between the fingers. Minerals in large pieces may be broken on an anvil with a hammer, the substance being wrapped in strong brown paper to prevent the fragments being scattered. In dealing with siliceous minerals and with certain iron ores, the fineness of the powder and careful mixing have a most important bearing not only upon the time spent in preparing a solution of the substance, but also upon the success of the analysis. Metals and alloys may be taken in the form of clippings, wire, foil, or sheet, or as filings, turnings, or borings. Small quantities of minerals should be crushed in a diamond mortar, which is placed on a solid block of wood and struck with a hammer (see Fig. 1). The small diamond mortar is in construction similar to the large instrument.

**Weighing.**—For simple experiments a good apothecary's balance, turning with  $\frac{1}{10}$  of a grain, is very convenient. For most analytical purposes a balance

which will turn with a milligram is sufficiently sensitive. The weights, for the sake of convenience, should diminish from 50 grams to 1 milligram. Each student should be provided with his own weights, and they should range at least from 10 grams downwards. Delicate balances should be constructed in the manner shown in Fig. 2.

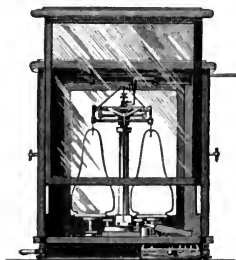


FIG. 2.—Balance.

This instrument will carry 200 grams in each pan, and turn with  $\frac{1}{10}$  of a milligram. The edges and planes upon which the beam and pans are supported are of agate. The beam is triangular in form, and made of aluminium-bronze gilt. When not in actual use the beam and pans are prevented from moving. The mechanism which allows of or arrests the movement of the balance is controlled by a handle seen on the left side. This position is so convenient that no fine balance should be purchased which has any other arrangement. Accuracy in weighing depends largely upon the ease and rapidity with which the operation is conducted. The observer should be comfortably seated, and should not be obliged to place the arms or hands in any constrained or awkward position. The light should fall on the instrument from the left-hand side, or from overhead, and full on the front of the balance case. At the back of the balance

should be a white wall or a screen of ground glass or paper. A special gas-lighting arrangement is made to fit on to the top of the balance if ordered, and it is found to be very convenient; it reflects the light down through the glass in the top of the case.

The quantity of substance to be taken for analysis depends very much upon the number of the constituents to be determined and the sensitiveness of the balance. The quantities usually weighed out are from 1 to 2 grams, and sometimes as much as 5 grams or even 20 grams. Substances should never be weighed while warm, and they should always be allowed to cool in an atmosphere free from moisture.

**Filtration.**—The best of filter papers should always be used. Those made by Schleicher and Schüll, No. 589, are most excellent, since they are almost free from ash, the lime salts having been extracted with hydrochloric, and the silica with hydrofluoric, acid. As they do not filter very fine precipitates well, it is sometimes useful to have a packet of No. 595, harder and closer grained paper. The most useful sizes are 9 and 11 cm. in diameter. The operation is greatly facilitated by boiling the liquid before precipitation (*when this is possible*) and filtering hot. It may be hastened by extracting air from a flask into which a solution is being filtered, so that the pressure of the atmosphere bears upon the liquid and forces it through the paper. For filtering under

pressure a water vacuum-pump is required ; furthermore, the filter-paper must be made to fit accurately to a funnel with perfectly straight sides inclined at an angle of  $60^{\circ}$ . It should be toughened by dropping strong nitric acid of 1.42 sp. gr. on to the apex of the filter. The filter is then filled with water, the air is exhausted from the flask with which it is connected, and in a

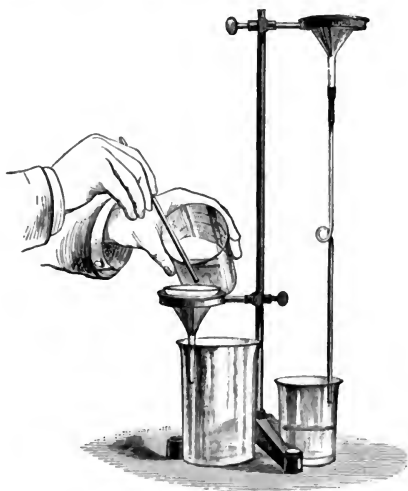


FIG. 3.—Decantation and Filtration.

minute or two the acid is washed out of the paper. The filtered water which is acid may be thrown away. Another quick filtering contrivance consists of a long glass tube (18 inches), with a loop in it ; it is connected

with the beak of the funnel by an india-rubber joint (Fig. 3). In order that it may work satisfactorily, water must be poured upon the filter as fast as it runs through, so as to keep the tube filled with running water; of course on this account the tube must not be too wide. The most convenient form of filter-pump is Arzberger and Zulkowsky's, as it works with water at low pressure, and there is no danger of water going over into the exhausted vessel.

**Ignition.**—Crucibles may generally be heated sufficiently strongly over a good Bunsen burner; when the temperature must be high, the crucible is surrounded by an iron jacket consisting of two hollow frustrated cones with their bases applied to each other. A still higher temperature is obtained with a gas blowpipe or a blast-lamp. It is very important in certain processes that no reducing gases from the flame gain access to the crucible, but at the same time it is necessary that the crucible be heated on its side. Reduction need not be apprehended if the tip of the flame only be allowed to enter the crucible.

## GENERAL DIRECTIONS.

1. Never weigh a substance directly on the pan of a balance, but always place it in a weighed watch-glass, a weighing-tube, test-tube, crucible, or some other vessel.

The object of this is twofold : first, to keep the balance clean ; secondly, to ensure correct weighings. When the balance is slightly out of equilibrium an incorrect weighing may be avoided by weighing the substance in a previously counterpoised vessel.

2. Be particular in arresting the balance before placing anything on the pans, or removing anything therefrom.

3. In placing weights upon the balance, do so in their regular order, beginning with the heaviest, and count their values from the empty places in the box. Check the values of the weights in returning them to their places.

4. Always heat your crucibles, allow them to cool in a desiccator, and weigh immediately before use ; even if the weight has been previously ascertained it should be verified.

5. Bear in mind that a weight wrongly recorded may destroy the entire value of an analysis.

6. Always pour reagents down the side of beakers or basins in order to avoid splashing.

7. In pouring liquids from a beaker, flask, or basin, the lip of the vessel should be slightly greased outside and up to the edge. Always place a glass rod against the lip of the vessel, so that it passes almost vertically below it for 2 or 3 inches (Fig. 3).

8. Do not use funnels which are fluted inside, or into which the filter paper does not fit closely.

9. Never pour a liquid on to the apex of a filter, but direct it against its side.

10. Always moisten filters before use.

11. Never use glass rods the ends of which are not rounded and smooth, otherwise they scratch the bottoms of beakers and render them liable to breakage.

12. When filtering into a beaker the tip of the funnel should touch the side of the vessel to avoid loss by splashes of liquid.

13. Never use rickety stands for filters or crucibles.

14. The work-table should be kept scrupulously clean and dry. As far as possible vessels containing liquids and funnels containing precipitates should be covered to keep out impurities. Funnels placed in the drying oven may be covered with paper.

#### CAUTION IN THE USE OF PLATINUM VESSELS.

15. A platinum crucible should never be used for the ignition of—

Reducible metallic compounds.

Arsenical compounds.

Caustic alkalies.

Alkaline nitrates.

Reducible and fusible phosphates.

16. Nitric acid should not be placed in platinum in presence of a chloride, nor should hydrochloric acid in

presence of a nitrate. These mixtures would dissolve some of the platinum.

17. Platinum vessels should always be cleaned after use and polished with carefully sifted, fine sea-sand. The particles of such sand have rounded edges, and so burnish rather than scratch the surface. Stains should be removed by fusing acid potassium sulphate in the crucible, or, if on the outside, by heating the crucible and dipping it into the powdered salt; that which adheres is fused by heat and allowed to run over the surface. Boiling in sulphuric acid is frequently efficacious.

18. A smoky flame should never be allowed to play upon a platinum vessel, nor a flame which shows by its colour that it contains zinc or copper.

19. Platinum should not be placed in contact with supports of galvanised iron, brass, or copper when heated; but iron triangles, covered with the stems of tobacco pipes, platinum foil, or asbestos cloth tied on with platinum wire, may be used. Best of all is a triangle of stout platinum wire. Ignited asbestos cardboard is a convenient flat support for hot crucibles to stand upon.

20. Crucible tongs should be tipped with platinum. Iron tongs may be used, provided they are kept well polished and that the tips are smooth. Pure nickel tongs are still better.



21. Every analysis of a mineral should be preceded by a very complete qualitative examination. Mistakes often occur through this preliminary analysis being neglected or not executed with sufficient care.

It will be seen by several of the examples which are quoted that many constituents occur in small quantities in minerals and alloys which would certainly have been overlooked had only the usual constituents been estimated.

#### DIRECTIONS FOR BURNING A FILTER.

It is advisable to proceed in the following manner. When the precipitate is dry, place the platinum crucible on a white plate of about 5 inches diameter, carefully remove the filter from the funnel, and gently squeeze it so as to loosen the precipitate. With great care shake out the precipitate into the crucible without spilling even the most minute particle. Such particles as may still adhere to the paper are loosened by gently rubbing the inner surfaces of the folded filter-paper together. Should some of the particles fall upon the plate, the crucible is transferred to a sheet of white or black glazed paper, and the particles are removed with a camel's-hair brush or a feather from the plate to the crucible. Should a particle or two fall on the paper it may in a similar manner be transferred to the crucible which has again been placed upon the plate. The filter

is then flattened so that the paper is folded in four, it is folded again so that the radius is doubled upon itself, and then it is rolled up very tightly and bound round with about 18 inches of some moderately thin platinum wire; the wire thus takes the form of a helix, with a straight piece projecting at either end. One of these ends should be 3 inches long at least. The filter is then held over the mouth of the crucible, and the flame of a Bunsen burner is applied to it until it has fairly taken fire; it is allowed to burn until the paper is consumed. There generally remains a skeleton of carbon, which requires the point of the Bunsen flame to be applied to ensure complete combustion. When the ash, shrunken within the helix of platinum, has become white or at least a light grey, the wire may be gently tapped on the edge of the crucible and the contents allowed to fall in. In the event of particles adhering to the wire, pull the two ends, and so open the helix slightly; this dislodges the ash if the wire is again gently tapped. Other particles adhering more firmly may be removed to the crucible either by means of a feather or camel's-hair pencil. The weight of the filter-ash is obtained by burning several filters one after the other, and weighing all the ashes in a crucible together.

### THE USE OF WEIGHED FILTERS.

Certain substances which cannot undergo calcination are collected on filters previously weighed, which are then weighed again. Filtration in such cases cannot conveniently be conducted with a filter-pump, as the toughening of the paper alters its weight. To dry the filter, fold it ready for use, and then place it on a watch-glass a little more than 2 inches in diameter, by the side of a beaker  $3\frac{1}{2}$  inches high and 2 inches in diameter. They stand on a clean sheet of paper in the water-bath. After being heated for two hours the filter is put into the beaker, covered with the watch-glass, allowed to cool in a desiccator, and weighed. The weighings are repeated half-hourly until the weight is constant. When the precipitate has been collected, the filter and contents are dried as far as possible in the funnel and then removed and folded up to be dried completely in the same manner as the empty filter.

Capsules for holding filters can be made by choosing two test-tubes of the largest size, one of which fits accurately within the other. The smaller tube is cut in two at 3 inches from the bottom, the larger at a distance of 2 inches. The bottom of the larger tube then makes an air-tight capsule to the other. The sharp edges of the glass should be gently heated in the lower

part of the mantle of a Bunsen flame so as to round them without distorting the glass by softening it too much.

### ATOMIC WEIGHTS.

The question as to the atomic weights to be employed in the necessary calculations is one which requires some consideration. We have four series of numbers: *First*, those in common use; *Second*, those based upon the accurate determinations of Stas; *Third*, those calculated by F. W. Clarke from the data of various investigators in which  $H = 1$  and  $O = 15.963$ ; and *Fourth*, the numbers derived in a similar manner by Van der Plaats, but with  $O = 16$ . For commercial purposes it is almost as necessary to use the ordinary atomic weights as it is to buy and sell by the legalised weights and measures. For scientific purposes it is of advantage to use those numbers which are known to be the most accurate; and as the substances to be weighed are oxides, sulphides, sulphates, or other oxidised compounds, it is more convenient to regard oxygen as having an atomic weight of 16 rather than 15.963.

The atomic weights variously appear thus:—

	(1) Commonly used.	(2) Revised Numbers.	(3) F. W. Clarke.	(4) Van der Plaats.
Mn	55	54.8	53.9	55
Fe	56	55.9	55.91	56
I	127	126.53	126.55	126.86
Al	27.5	27.32	7.01	27.08
Pt	197	196.7	194.41	194.9
K	39	39.04	39.02	39.144
Cr	52.5	52.4	52.01	52.3
Cu	63.5	63.0	63.17	63.33
Cl	35.5	35.37	35.37	35.456

With Fe and K there will be no serious error introduced by the use of one or other of the series of numbers, but the atomic weights of the other elements differ more widely. To obviate difficulties, wherever a calculation appears, the atomic weights used will be quoted. The atomic weights, according to Van der Plaats, are given at the end of the volume.

### REAGENTS.

All the solutions used as reagents are made as far as possible of such a strength that they contain reacting weights in equal volumes.

Thus 1 litre of sulphuric acid, unless specified as strong acid or as oil of vitriol, contains 98 grams of  $\text{H}_2\text{SO}_4$ .

This quantity will react with barium-chloride solution, volume for volume, or, in other words, the barium chloride contains 208 parts of  $\text{BaCl}_2$  per litre. This will liberate 71 parts of  $\text{HCl}$ , and accordingly the hydrochloric acid, unless otherwise specified, contains 71 parts  $\text{HCl}$  per litre, which in turn reacts with 56 parts  $\text{CaO}$  to form  $\text{CaCl}_2$ . The solution of potash contains 94 parts  $\text{K}_2\text{O}$  per litre, or the quantity which will exactly neutralise the sulphuric and the hydrochloric acids. These weights may be expressed thus—

$$\frac{\text{H}_2\text{SO}_4}{1000} = \frac{98 \text{ parts}}{1000}$$

$$\frac{2\text{HCl}}{1000} = \frac{71}{1000}$$

$$\frac{\text{BaCl}_2}{1000} = \frac{208}{1000}$$

$$\frac{\text{K}_2\text{O}}{1000} = \frac{94}{1000}$$

$$\frac{2\text{HNO}_3}{1000} = \frac{126}{1000}$$

In many cases it is found very convenient to roughly weigh out quantities of reagents in the solid form, and to dissolve in water immediately before use. But it is more advantageous to use measured volumes of solutions of known strength.

## INTRODUCTORY EXAMPLES.

By performing the simple analytical processes which will now be described, it is easy to realise the meaning of the atomic weights and equivalent weights, and within certain limits to verify the following numbers.

All the weighings excepting those in **Example 4** were made with a good pair of apothecary's scales.

	Atomic Weights.	Equivalent Weights.
Silver . .	108	108
Magnesium . .	24	12
Lead . .	207	103.5
Iron . .	56	28
Copper . .	63.3	31.65
Oxygen . .	16	8
Zinc . .	65.3	32.65

## 1. DETERMINATION OF LEAD IN LITHARGE.

Take a piece of hard glass-tube 10 inches long and half an inch to an inch in diameter, of the kind known as "combustion-tube," draw out the tube in the middle into two, and seal one end of each so as to make two strong test-tubes. Sometimes moisture condenses within

the tubes ; dry by making them hot, and sucking out air with another tube.

Draw out a piece of the same tube so as to taper at each end to about  $\frac{1}{8}$ th of an inch in diameter ; that portion in the middle which does not taper need not be more than  $\frac{1}{2}$  an inch in length. One of the taper ends is now made about an inch long, the other 3 inches. The former is intended to be adapted to an india-rubber-tube connected with the gas supply ; the latter is intended to fit into the test-tube ; the thick portion forms a loose-fitting stopper. Weigh the test-tube, and into it put sufficient litharge to increase its weight by 2.23 grams. Place the tube in a stand in a position almost horizontal, pass in a current of coal-gas, and heat the litharge at first gently, holding the gas-burner in the hand and keeping the flame in motion. Finally, when it is seen that lead is formed in some quantity, heat strongly to melt it into globules, cool in the current of gas, and weigh. When the weight of the tube has been deducted the lead should weigh 2.07 grams.

	Grams.
Weight of tube + litharge . . . .	= 15.44
Weight of tube . . . . .	= 13.21
	<hr/>
Weight of litharge	= 2.23
	<hr/> <hr/>



After reduction in coal-gas—

Weight of tube + lead . . . = 15.28

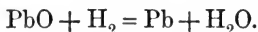
Weight of tube . . . = 13.21

Weight of lead = 2.07

Atomic weights, Pb = 207, O = 16.

	Found.	Calculated.	} Composition of litharge.
Lead oxygen	. 207	207	
O . . .	. 16	16	
	<u>223</u>	<u>223</u>	

The reaction—



$$223 + 2 = 207 + 18.$$

## 2. DETERMINATION OF THE WEIGHT OF MAGNESIUM EQUIVALENT TO 108 PARTS OF SILVER.

Take some perfectly bright magnesium ribbon, or clean some that is tarnished with fine sand or glass paper. Heat a porcelain crucible or small porcelain basin,  $2\frac{1}{4}$  to  $2\frac{3}{4}$  inches in diameter, over a gas-lamp for two minutes, and allow it to cool. While it is cooling weigh out roughly 2 grams of silver nitrate, and dissolve in not less than 20 c.c. of distilled water. Weigh the crucible with-

out lid, place about 15 inches of magnesium ribbon in the crucible and weigh again, take exactly 0.12 grams. Transfer the silver-nitrate solution to the crucible, break or cut off pieces of the magnesium an inch in length, and add them to the solution in the crucible until all have completely dissolved and powdery metallic silver has separated. A very light piece of glass rod, with the ends rounded, about  $2\frac{1}{2}$  inches in length, is used for stirring the magnesium and liquid together, and keeping the metal immersed below the solution. It will be observed that the reaction causes the liquid to become warm. As particles of silver sometimes accumulate upon the glass rod, do not remove it from the liquid. When all the magnesium appears to have been dissolved, the liquid is gently heated to near boiling, and the metallic particles are allowed to settle. The liquid is then decanted on to a small filter, to retain any particles of silver; as far as possible this should be done without disturbing the precipitate. Add about 20 c.c. of distilled water to the crucible, stir up the silver, allow it to settle, decant again, and repeat this ten times. The first two decantations contain silver nitrate in considerable quantity, and should be saved in a bottle labelled "SILVER RESIDUES." The latter washings must be tested for silver by a drop of hydrochloric acid, which will give no turbidity if all the soluble salts have been removed.

The crucible containing the washed precipitate of silver is now placed on a piece of wire gauze and gently heated by the flame of a Bunsen, which is kept in the hand, and gently moved to and fro. The heat should be moderated by removal of the flame, if there be any tendency to boiling or sputtering. After a few minutes the precipitate will be dry enough to heat more strongly over a gas-burner for five minutes. The increased temperature will change the grey colour of the precipitate to that of frosted silver.

The crucible and contents are then allowed to cool and afterwards weighed. The small amount of pulverulent silver collected on the filter is washed two or three times with warm water. Remove the filter from the funnel when the whole of the liquid has drained away, and place it on a clean clay triangle, so that it is supported in the position in which it was held in the funnel. Dry the paper by waving the flame of a Bunsen burner beneath, and occasionally blowing upon it as long as steam comes off, then fold it up ready for burning.

Should the filter scorch or take fire, this will almost surely happen at the apex. Remove it without delay, flatten the filter, double the apex over, and extinguish by folding the paper again. Wrap up the filter into a little roll, hold it gently by one edge with a pair of nickel crucible tongs or forceps of iron carefully brightened, hold it over the crucible, and with the gas-burner in the

left hand apply the tip of the flame to the paper, allow it to burn away and the globules of silver to fall into the crucible. Ignite the crucible and contents during two or three minutes. Let the crucible cool, and weigh it again. The total weight of the silver should be approximately 1.08 grams.

*Example—*

Weight of crucible + silver . . . = 30.14

Weight of crucible . . . . . = 29.12

Weight of silver in crucible = 1.02

Weight of crucible + silver in crucible + silver on filter . . . = 30.19

Weight of crucible . . . . . = 29.12

Total weight of silver = 1.07

Atomic weights, Ag = 108, Mg = 24.

The reaction—



$$2(170) + 24 = 2(108) + 86.$$

Hence 12 parts of magnesium are equivalent to 108 parts of silver.

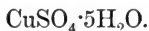
	Equivalent Weights.	
	Found.	Calculated.
Silver . . . . .	107	108
Magnesium . . . . .	12	12

*Notes.*—(1.) When a filter is used it should fit accurately into a funnel  $\frac{1}{4}$ th of an inch larger, in order that it may be washed thoroughly. This is impossible if the paper projects above the edge of the funnel.

(2.) In decanting, slightly grease the forefinger and rub it against the edge of the vessel, apply a stirring rod to the greased edge, and pour the liquid down the rod on to the filter or into a beaker glass (Fig. 3, p. 12).

(3.) The silver is easily removed from the crucible. Should any particles adhere they may be dissolved out with nitric acid.

### 3. DETERMINATION OF WATER & COPPER IN CRYSTALS OF COPPER SULPHATE



Take a glass tube like that used for the determination of lead in litharge, and weigh it. Select some crystals of pure copper sulphate (see **Example 4**), powder, and dry them by pressure between folds of blotting-paper. Weigh in the tube 2.49 grams of the salt. Place the tube in a clip in a horizontal position and heat the greater part of the tube, and particularly the end containing the salt, by passing the flame of a gas-burner along it.

Now heat the salt, keeping the flame in motion ; a considerable quantity of water is set free, which must not be allowed to collect in the tube, but is removed as vapour by passing a tube bent at right angles into that which holds the copper salt, and withdrawing air by a water aspirator or by the mouth. The bent tube may be  $\frac{1}{4}$ th of an inch in diameter. When the copper salt has almost lost its blue colour, and is nearly white, remove the gas-flame and continue to suck out air until the tube remains dry, then resume heating, the flame being kept in motion until the air which is sucked into the mouth begins to taste of sulphurous acid. Now remove the lamp, and continue withdrawing air until the contents of the tube are white and dry. Allow to cool, and weigh. The tube contains anhydrous copper sulphate. The weight should be 159 grams. After weighing, heat very strongly, passing coal-gas into the tube in the manner directed for the estimation of lead in litharge. When no more water is seen to be disengaged, remove the lamp, cool in a current of coal-gas, and weigh. The contents of the tube are metallic copper. Should the weight be too large, replace the tube supplying coal-gas, turn on the tap, and commence to heat. Continue a red-heat for ten minutes, remove the flame, and allow to cool in a stream of gas, weigh again.

The weight of metallic copper should be between 63 and 64.

*Example—*

2.49 grams of copper sulphate were taken.

	Grams.
Weight of tube + copper sulphate	= 23.16
Weight of tube . . . . .	= 20.67
	<hr/>
(a) Weight of copper sulphate	= 2.49
	<hr/> <hr/>

After heating—

Weight of tube + copper sulphate	= 22.26
Weight of tube . . . . .	= 20.67
	<hr/>
(b) Anhydrous copper sulphate	= 1.59
	<hr/> <hr/>

After ignition in coal-gas—

Weight of tube + copper . . . . .	= 21.31
Weight of tube . . . . .	= 20.67
	<hr/>
Metallic copper	= 0.64
	<hr/> <hr/>

(a) Weight of copper sulphate crystals . . . = 2.49

(b) Weight of anhydrous copper sulphate . . = 1.59

Combined water	= 0.90
	<hr/> <hr/>

Exact composition of copper sulphate—

Copper sulphate crystals $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	{	Cu = 63·3	} Anhydrous copper sulphate $\text{CuSO}_4$
		S = 32	
		$\text{O}_4 = 64$	
		<hr/> 159·3	
		$5\text{H}_2\text{O}$ 90·0	
		<hr/> 249·3	
		<hr/> <hr/>	

	Found.	Calculated.
Anhydrous copper sulphate = 159 parts		159·3
Water : . . . = 90 „		90·0
Metallic copper . . . = 64 „		63·3

*Note.*—Copper sulphate loses all its combined water when heated above  $240^\circ \text{C}$ . At higher temperatures it decomposes, yielding sulphur dioxide, copper oxide, and oxygen; but in presence of hydrogen or coal-gas it yields metallic copper, and water is formed from the oxygen combining with the hydrogen of the gas.



#### 4. THE DETERMINATION OF THE COMPOSITION OF COPPER OXIDE.

**Preparation of Pure Copper Sulphate.**—Recrystallise some copper sulphate in order to free it from impurities, proceeding in the following manner :—Take 40 grams of the crystallised commercial salt and boil with 50 c.c. of water, to which a few drops of nitric acid have been added, in order to peroxidise any ferrous sulphate which may be present. Filter if the liquid is not quite clear, and boil for ten minutes. The liquid is then allowed to cool in an evaporating dish, crystals separate, and from these the mother-liquor is drained, by tilting up the dish on the mouth of a beaker-glass. Separate the crystals with a stirring rod, and drain them on several folds of blotting-paper, then gently press them between folds of fresh paper.

**Preparation of Pure Copper Oxide.**—Take 10 grams of the purified copper sulphate dissolved in a beaker-glass in 50 c.c. of water, and while boiling add very cautiously thereto a solution of sodium carbonate until no further precipitation of the black cupric oxide occurs. The precipitate is separated from the supernatant liquid by decantation and then washed with boiling water, the washings being decanted after the precipitate has settled. When this process has been repeated two or

three times, the precipitate may be washed out of the beaker on to a previously well-moistened filter. The precipitate is washed on the filter until the filtrate is no longer alkaline to red litmus or turmeric paper. Dry the precipitate on the filter in a water-oven or in a current of hot air; transfer the dried precipitate to a porcelain crucible and ignite to convert any carbonate present into black cupric oxide, and to remove the last traces of moisture. In order to facilitate drying, the filter may be removed from the funnel by loosening it and tenderly lifting it out by that side of the paper which is doubly folded. It may be placed in an evaporating basin sufficiently large, and this made to rest on a beaker in which water is boiling. As in the previous case, the dried precipitate may be removed from the filter-paper and ignited.

### **Determination of the Copper in Copper Oxide.**

—This experiment may be made with advantage if the weighings are performed with a delicate balance. Weigh in a glass tube, with a gas delivery-tube attached (**Example 1**, p. 23), a quantity of copper oxide, rather more than 0.793 gram. Fix the tube in a stand and heat the copper oxide to redness; probably a little moisture will be expelled; suck air out of the tube by means of a smaller tube, bent at right angles, in order to dry the powder completely. Cool in a desiccator, and, with the flattened end of a wire or the blade of a pen-

knife, remove enough of the copper oxide to reduce its weight to 0.793 gram exactly. Attach the coal-gas tube, and pass a fairly-rapid current of gas into the tube and heat the copper oxide to redness. After a short interval steam is seen to be given off, then the copper oxide glows to bright redness, much water and steam pass away (the water should not be allowed to condense in sufficient quantity to run down the sides of the tube), and after a time the copper ceases to glow, but heating is continued a little longer until the metallic copper shrinks. Cool, without admitting air, by continuing the current of coal-gas, and weigh.

*Example—*

Weight of tube empty . . . = 16.020

Weight of copper oxide . . . = 0.793

Weight of tube + copper oxide = 16.813

After heating to redness for five minutes the weight was a few milligrams less, but it was made up to 16.813, with 1 or 2 milligrams of copper oxide.

After ignition in coal-gas—

Weight of tube + copper . . . = 16.653

Weight of tube . . . = 16.020

Weight of copper = 0.633

Hence the composition of copper oxide is—

	Found.	Calculated.
Copper . . .	63·3	63·3
Oxygen . . .	16·0	16·0
	<hr/>	<hr/>
	79·3	79·3
	<hr/>	<hr/>

The reaction—



$$79·3 + 2 = 63·3 + 18.$$

## 5. DETERMINATION OF THE WEIGHT OF COPPER EQUIVALENT TO 108 PARTS OF SILVER.

Weigh a porcelain crucible of the capacity of about 20 c.c., or larger. Weigh in the crucible some perfectly bright fine copper wire which has been wrapped round a pencil and made into a little skein. The copper should weigh 0·316 gram, or, if the balance be not sufficiently delicate, 0·32 gram. Then weigh in the crucible 2 grams of silver nitrate, add 10 c.c. of water, place the crucible on a triangle, and heat it by keeping a gas flame moving beneath it. As soon as all the silver nitrate has dissolved, drop in the copper wire and let it remain tranquil for some time. The silver separates in very beautiful crystals. Stir the liquid and silver with a

small light glass rod, and endeavour to ascertain whether there be any little rings of copper still unacted on. When it is evident that all has been dissolved, carefully decant the solution of copper on to a previously well-moistened filter, wash the precipitate with water, and test occasionally for an excess of silver in the filtrate by adding a drop of hydrochloric acid to about 10 drops of the filtered liquid which has been collected in a clean test-tube for the purpose. After the fifth or sixth washing and decantation, a little ammonia may be added to the washing water in the crucible and left for some minutes, with an occasional stirring. The ammonia will probably cause a blue coloration, and when this ceases to become darker it may be decanted into a beaker, and the washing resumed in the same way and continued until the washing water remains colourless.

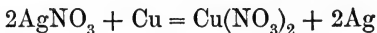
If the decanted liquid contains any minute particles of silver it may be poured on to the filter.

While the washing with ammonia has been in progress, the filter has in the meantime been well washed with distilled water several times, to remove the copper salt from the paper, and if any persistent light blue stains are seen they may be removed by washing with dilute hydrochloric acid poured from a test-tube; after once more washing with water to remove the acid, the ammoniacal solution may be filtered.

Dry the silver and treat the filter-paper in the manner already described (p. 27).

The total volume of the washings and original filtrate will measure about 400 c.c.

The reaction—



$$2(170) + 63.3 = 187.3 + 2(108);$$

hence 63.3 parts of copper = 2(108) of silver,

and 31.6 parts of copper = 108 of silver.

*Example—*

	Grams.
Weight of crucible . . .	= 10.92
Weight of copper . . .	= 0.32
	<hr/>
Weight of crucible + copper	= 11.24
	<hr/>
Weight of crucible + silver . .	= 12.00
Weight of crucible . . .	= 10.92
	<hr/>
Weight of silver	= 1.08
	<hr/>

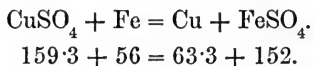
	Equivalent Weights.	
	Found.	Calculated.
Silver . . .	108	108
Copper . . .	32	31.6

## 6. DETERMINATION OF THE WEIGHT OF IRON EQUIVALENT TO 108 PARTS OF SILVER OR 31.65 OF COPPER.

Weigh a porcelain crucible 2 inches in diameter, and in it weigh 0.56 gram of fine iron wire which has been brightened by emery cloth or glass paper, and afterwards wrapped round a pencil. Remove the wire, and boil 5 grams of copper sulphate in the crucible, with 10 or 12 c.c. of water acidified with 5 or 6 drops of dilute sulphuric acid (1 volume oil of vitriol to 5 of water), and when all is dissolved drop the iron wire into the hot liquid. Allow it to remain tranquil for about half an hour, until it appears to have been all dissolved. Then crush up the copper with a glass rod, and so detach it from any remaining particles of iron, and warm gently for a few minutes. The copper is capable of being washed by decantation without loss if the precipitation has been carried out in the manner described. The washings need not be passed through a filter, but poured directly into a beaker. After the washings cease to give a blue colour when a drop is let fall on to a spot of a solution of potassium ferri-cyanide (showing that there is no more ferrous sulphate present), the liquid may be decanted away, and any particles of copper in the beaker may be washed as before and finally returned to the

crucible with about 25 c.c. of pure alcohol or redistilled methylated spirit. Decantation and renewed washing with alcohol must be continued about three times, so that all the water is removed and the copper easily dried. To dry the copper, the crucible may be placed in the mouth of a small beaker in which water is boiling. Or a cork is fitted to a flask, and the tube of a funnel passed through the cork; water is kept boiling vigorously in the flask, and the crucible is placed in the funnel. In ten minutes the contents of the crucible will be quite dry. Wipe the outside of the crucible with a linen cloth, weigh, and heat again until the weight is constant.

The reaction—



Hence 56 parts of iron are equivalent to 63.3 of copper, but 63.3, the atomic weight of copper, is equivalent to 2(108) parts of silver (p. 38); therefore the half of 56 or 28 parts of iron are equivalent to 108 of silver.

*Example—*

	Grams.
Weight of crucible . . .	= 29.12
Weight of iron . . .	= 0.56
	<hr/>
Weight of iron + crucible	<u>= 29.68</u>



Weight of crucible + copper . = 29.76

Weight of crucible . . . = 29.12

Weight of copper = 0.64

		Found.	Calculated.
Atomic weights	{ Iron .	56	56
	{ Copper .	64	63.3
Equivalent weights	{ Iron .	28	28
	{ Copper .	32	31.6

*Notes.*—(1.) As copper is oxidisable below a red-heat, the precipitate cannot be safely dried over a lamp; and, for the same reason, the precipitate could not be collected on a filter and burnt without incurring some trouble in reducing the burnt copper. Copper burns to copper oxide, but silver under similar circumstances does not burn.

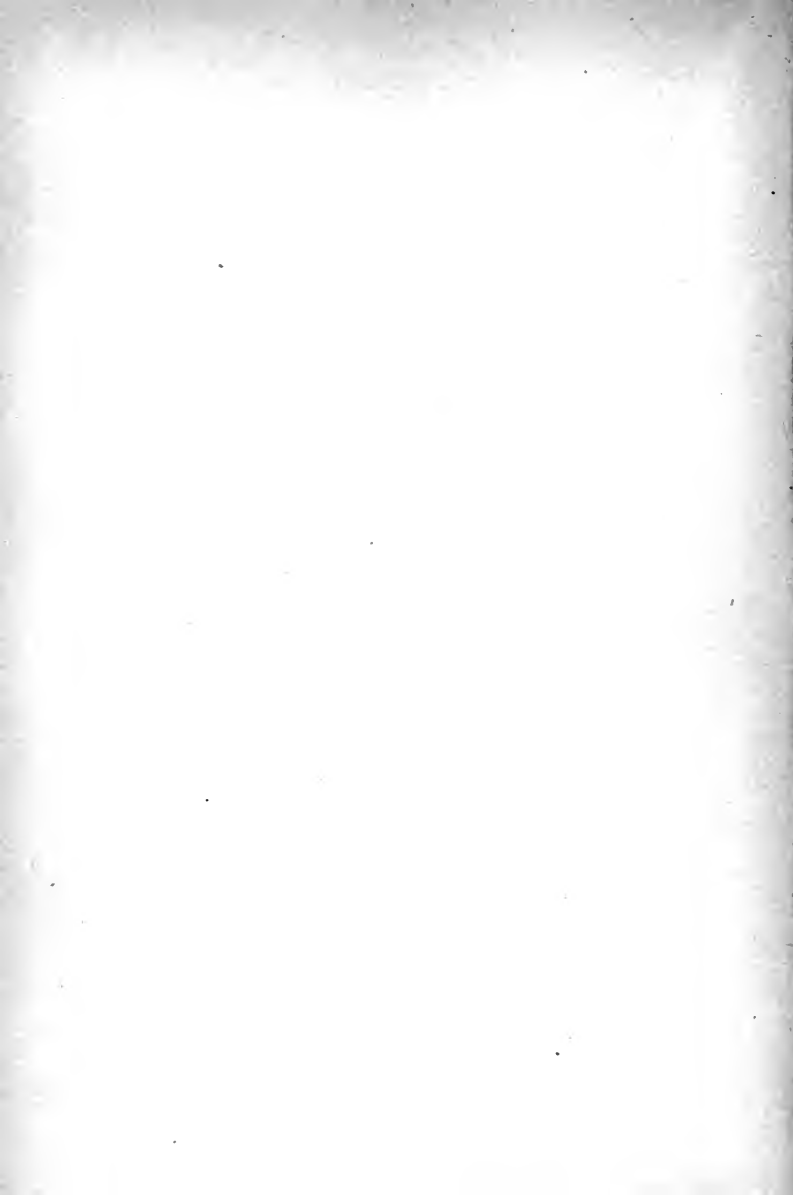
(2.) A copper salt is apt to deposit a hard and continuous layer of copper on iron wire; such a coating is formed when pure copper sulphate in a cold solution acts upon iron. Hence it is necessary to heat the liquid, to make it acid, and to crush up the copper so as to bring any fragments of iron wire unacted on into contact with the liquid. When the result is not good, examine the copper under a microscope of low power, or with a powerful lens.

- (3.) The proper quantity of sulphuric acid to be added should be attended to ; if too little, the deposit is not sufficiently crystalline to become detached from the iron ; if too much, hydrogen instead of copper will be displaced by a part of the iron being dissolved in the acid. No gas bubbles should be seen to come from the liquid.
- (4.) As the purest iron wire contains some carbon, and only 99·5 per cent of iron, the result can never be quite exact, even if executed with the greatest care, unless this fact is taken into account. The following calculation shows the weight of such iron that should be taken :—

$$\frac{100 \times \cdot 56}{99\cdot 5} = \cdot 5628.$$

- (5.) Should particles of copper float on the surface of the liquid during the process of washing, they may generally be made to sink by pouring a few drops of ether on to the surface and then adding a drop of alcohol. The particles then sink if slightly agitated with a glass rod.

ESTIMATIONS OF MINERAL  
CONSTITUENTS



## 7. ESTIMATION OF SODIUM IN ROCK-SALT.

**Estimation of Moisture.**—Heat a large porcelain crucible, size No. 1, about 2 inches in diameter, cool it in a desiccator, and weigh. Roughly weigh and place in the crucible 2 grams of perfectly colourless and transparent rock-salt in powder. Weigh again accurately, the crucible being covered by the lid. As much as 25 grams may be taken for the estimation of moisture, and with advantage. Heat the covered crucible, gently at first, then at a higher temperature. Remove the cover and continue the heat for five minutes. Cool the covered crucible in a desiccator, and weigh. The loss of weight is moisture.

**Estimation of the Sodium.**—The salt is converted into neutral sulphate.

Proceed in the following manner :—

Dissolve the salt by the addition of half an ounce, or about 15 c.c. of water, mix it carefully, drop by drop, with not less than 20 drops of concentrated oil of vitriol (sp. gr. 1·8), and evaporate at a temperature below boiling until no more fumes are evolved, then cautiously heat the crucible above a Bunsen burner in a draught chamber until white fumes of sulphuric acid are no longer dis-

engaged. It is necessary to ensure the presence of an excess of acid by adding a few drops more if it appears necessary. The crucible is closed by its cover, and heated strongly for a few minutes; after cooling, a little powdered ammonium carbonate is sprinkled on the contents in order to convert any acid sodium sulphate into the neutral salt, and heat is again applied strongly. After cooling, the crucible is once more weighed, the weight of the empty crucible being deducted; the difference is normal sodium sulphate.

*Example.*—Rock-salt. The estimation of moisture—

$$\text{Weight of crucible + salt} \quad . \quad . \quad = 83.6765 \text{ (a)}$$

$$\text{Weight of crucible} \quad . \quad . \quad = 60.1581$$

$$\text{Weight of rock-salt} \quad = \underline{\underline{23.5184}}$$

After heating—

$$\text{1st weighing} \quad . \quad . \quad = 83.6580$$

$$\text{2d} \quad ,, \quad . \quad . \quad = 83.6578 \text{ (b)}$$

$$\text{(a) } 83.6765$$

$$\text{(b) } 83.6578$$

$$\text{Water} \quad = \underline{\underline{0.0187}}$$

$$\frac{0.0187 \times 100}{23.5184} \quad \begin{array}{l} \text{Per cent.} \\ = \underline{\underline{0.079 \text{ moisture}}} \end{array}$$

**The Estimation of Sodium.**—About 2 grams of the dried salt were converted into sulphate.

$$\text{Weight of crucible + salt} \quad . \quad = 62.4782$$

$$\text{Weight of crucible} \quad . \quad . \quad = 60.1610$$

---


$$\text{Weight of salt} \quad = \underline{\underline{2.3172}}$$

$$\text{Weight of crucible + sodium sulphate} \quad . \quad = 62.970$$

$$\text{Weight of crucible} \quad . \quad . \quad . \quad = 60.161$$

---


$$\text{Weight of sodium sulphate} \quad = \underline{\underline{2.809}}$$

$$\text{Na}_2 = 46$$

$$\text{S} = 32$$

$$\text{O}_4 = 64$$

---


$$\begin{array}{rcl} 46 \times 2.809 \times 100 & \text{Per cent.} & \\ \hline 142 & \frac{46 \times 2.809 \times 100}{142 \times 2.3172} = & 39.29 \text{ sodium.} \end{array}$$

---


$$\text{Found.} \quad \text{Calculated.}$$

$$\text{Sodium in sodium chloride} = 39.29 \quad 39.31 \text{ per cent.}$$

*Note.*—The size of the crucible and quantity of the materials used are duly proportioned to the weight of salt taken. If a smaller crucible is used the quantity of salt must be reduced.

## 8. ESTIMATION OF CHLORINE.

Rock-salt, NaCl. Sylvine, KCl.

Carnallite,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

About 1 gram of the powdered salt is accurately

weighed and gently ignited in a previously weighed porcelain crucible; the loss of weight represents water (see **Example 7**). The crucible should at first be covered to prevent particles of the salt being projected out. The salt is then emptied into a beaker and the crucible rinsed out with hot water, the rinsings being added to the beaker. About 100 c.c. of water are thus added, the solution is acidified with nitric acid, and the chlorine precipitated as silver chloride by the addition of silver nitrate as long as any precipitate is formed. The liquid is boiled for a few minutes and well stirred with a glass rod to make the silver chloride collect in curdy masses. Decant the clear liquid and wash the precipitate with water twice or thrice by decantation. The liquid is filtered through a filter 4 inches in diameter; the silver chloride is well washed on the filter with distilled water and dried; it is next removed from the paper to a previously weighed porcelain crucible and heated until it fuses. The paper is then folded and tightly rolled up; and at one end—that is to say, at the edge of the paper, away from the apex of the filter—the roll is bound round with platinum wire.

Holding the paper over the crucible by the wire, it is set on fire by a Bunsen flame and allowed to burn until it falls into the crucible. The crucible is then heated, and the filter-ash is touched with a drop of fuming nitric acid, which consumes any remaining carbon. But



the silver chloride on the paper has been reduced to the state of metal; one drop more of nitric acid is therefore added, and the crucible is very gently heated until no further action is observed; this changes the metallic globules into silver nitrate; then a drop of hydrochloric acid is added which converts the nitrate into chloride and destroys the nitric acid; the liquid is evaporated on a water-bath and cautiously heated over a lamp till acid fumes are no longer disengaged; the temperature may then be raised until the silver chloride begins to melt. The crucible is cooled and weighed. To clean the crucible add about  $\frac{1}{2}$  c.c. of dilute sulphuric acid and a piece of zinc; this will reduce the chloride to the state of pulverulent silver, which may easily be washed out.

*Notes.*—(1.) Care must be taken not to heat the solution mixed with nitric acid before the silver nitrate has been added in excess.

(2.) If the filter-paper be bound round with platinum wire there is a risk of a little silver chloride being reduced to the state of metal in contact with the platinum, in which case it would be lost. Furthermore, the reduced silver would form an alloy with the platinum, and the piece of wire would be spoilt.

*Example.*—Two samples of rock-salt were analysed—

	I.	II.
Weight of salt taken . . .	= 0·6790	0·4374
Weight of crucible + AgCl + filter-ash =	18·8698	18·2820
Weight of crucible . . . =	17·2083	17·2077
	<hr/>	<hr/>
	1·6615	1·0743
Weight of filter-ash . . . =	0·0065	0·0025
	<hr/>	<hr/>
Silver chloride	= 1·6550	1·0718
	<hr/>	<hr/>

Ag = 108·0

Cl = 35·5

$$\frac{35 \cdot 5 \times 1 \cdot 655 \times 100}{143 \cdot 5 \times 0 \cdot 679} = \text{I. Per cent. } \underline{\underline{60 \cdot 29 \text{ chlorine}}}$$

$$\frac{35 \cdot 5 \times 1 \cdot 0718 \times 100}{143 \cdot 5 \times 0 \cdot 4374} = \text{II. Per cent. } \underline{\underline{60 \cdot 619 \text{ chlorine}}}$$

If the atomic weight 35·4 be accepted for chlorine, then the calculations above give—I. 60·17 per cent, and II. 60·49 per cent, of chlorine.

In a previous example the moisture and sodium were determined ; hence we find the complete analysis of rock-salt to give the following numbers :—

	Found. Per cent.	Calculated for NaCl. Per cent.
Moisture . . .	0·079	...
Sodium . . .	39·29	39·32
Chlorine . . .	60·619	60·68
	<u>99·988</u>	<u>100·00</u>

## 9. ESTIMATION OF SULPHURIC ACID.

Epsom salts,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . Sodium sulphate or Glauber's salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . Copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . Dilute sulphuric acid.

Dissolve from 0·5 to 1 gram of the salt in 150 c.c. to 200 c.c. of water in a beaker of 400 c.c. capacity, add a few drops of hydrochloric and boil. Boil a solution of barium chloride, and add this gradually to the boiling solution of the salt as long as a precipitate falls. The precipitate is barium sulphate, and when an excess of barium chloride has been added, the whole of the sulphuric acid has been removed from the solution. The liquid, after boiling for a few minutes, is allowed to stand until the precipitate has settled down and left a clear solution. A filter of Swedish paper is then neatly fitted into a funnel of such a size that there is a rim of glass of about a quarter of an inch, extending above the

rim of the filter-paper ; this is moistened with hot distilled water, placed in a filter stand with a beaker beneath it, somewhat larger than that used for the precipitation. The beak of the funnel must touch the side of the beaker-glass, so that the liquid runs down it and does not cause the filtered solution to splash.

The clear solution is decanted by pouring it down a glass rod held at the edge of the beaker and directed on to the filter-paper. When the liquid has run through, the precipitate is washed with a stream of hot distilled water from a wash-bottle and poured on to the filter, which must not be more than half filled. When the whole of the precipitate has been carefully rinsed on to the filter it must be washed with hot water. The filtrate is now tested from time to time by collecting a little in a clean test-tube and adding a drop of sulphuric acid, and when no more turbidity is caused by this addition, all the excess of barium chloride, with other soluble salts, may be considered to have been washed away. The filter is then dried in a water-oven or in a current of warm air. It is advisable, during the drying process, to cover the mouth of the funnel with a piece of common white filter-paper, which is folded over the edges of the glass in order to keep out dust and dirt. When dry, the filter may be removed from the funnel, folded up very tightly, placed in a previously weighed porcelain or platinum crucible of about 1 ounce capacity, and burnt completely.

In igniting a precipitate in this manner, the crucible should be supported on a triangle of platinum or of iron wire covered with pipe-clay, such as pieces of the stems of a large tobacco pipe. The crucible should be inclined at an angle of about  $45^{\circ}$  or more, and the lid should rest against the inner edge of the crucible (Fig. 4). A smokeless Bunsen burner should be used, and the flame, striking the under edge of the lid, should play on to the precipitate contained in the crucible. When all the carbon is burnt off, and the barium sulphate is quite white, the crucible is allowed to cool slightly; it may then be transferred by means of crucible tongs to a triangle placed in a desiccator, the air of which is dried by a dish of sulphuric acid. The crucible tongs should be absolutely clean. If such tongs are not at hand, it is better to allow the crucible to cool, so that its warmth is not inconvenient, and then to take it in the fingers, which must, of course, be carefully cleaned and dried.

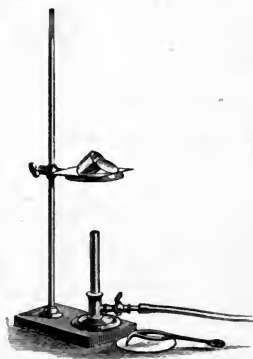


FIG. 4.—Crucible ready for ignition.

The crucible and contents are accurately weighed when quite cold; deduct the weight of the crucible, and

the excess is barium sulphate + filter-ash ; the weight of the latter must be deducted.

*Example—*

	Grams.
Copper sulphate taken . . . . .	= 1.056
Weight of crucible and barium sulphate . . . . .	= 43.954
Weight of crucible . . . . .	= 42.963
Barium sulphate + filter-ash . . . . .	= 0.991
Weight of filter-ash . . . . .	= 0.006
Actual weight of barium sulphate	<u><u>= 0.985</u></u>

Where Ba = 137, S = 32, and O = 16.

BaSO <sub>4</sub> = 233	Ba = 137	S = 32
	S = 32	
and SO <sub>3</sub> = 80	O <sub>4</sub> = 64	O <sub>3</sub> = 48
	<u>233</u>	<u>80</u>
	<u><u>233</u></u>	<u><u>80</u></u>

To find the SO<sub>3</sub> in 0.985 gram of BaSO<sub>4</sub>—

$$\frac{80 \times 0.985}{233} = 0.3382 \text{ gram SO}_3.$$

To find the percentage of SO<sub>3</sub> in 1.056 grams of CuSO<sub>4</sub>·5H<sub>2</sub>O—

$$\frac{0.3382 \times 100}{1.056} = 32.02 \text{ SO}_3 \text{ Per cent.}$$

The quantities may thus be stated—

	Found.	Calculated.
SO <sub>3</sub>	32.02	32.10 per cent.

*Notes.*—(1.) In the precipitation of sulphuric acid, hydrochloric acid is added to ensure the precipitate containing nothing but barium sulphate, and the liquid is heated in order that, according to experience, the precipitate may settle and be filtered easily.

- (2.) It is desirable not to use a large excess either of hydrochloric acid or of barium chloride, because barium sulphate is not altogether insoluble in hot acids, and it has a tendency to carry down salts, especially nitrates and chlorides, which cannot be removed by washing. This is especially the case when iron is present.
- (3.) The rapid filtration of barium sulphate is best facilitated by attaching to the beak of the funnel, with a piece of india-rubber tube, a glass tube 18 inches long, with a loop in it (Fig. 3). A continuous stream of liquid then passes through the paper if it be made to fit the funnel accurately.

## 10. ESTIMATION OF COPPER AS CUPRIC OXIDE

Copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

Crush some selected crystals of the salt and press the powder between folds of blotting-paper to remove adhering moisture. Place the powder in a corked test-tube. Weigh out from 0.5 to 1 gram of the powder, and dissolve it in 200 or 250 c.c. of water. Boil the liquid, and add while boiling a considerable excess of pure caustic soda (or potash), which at once precipitates the black cupric oxide. The liquid is decanted on to a filter as soon as the precipitate has settled. The filter must be smaller by a quarter of an inch than the funnel, and the liquid must not more than half fill the filter. The precipitate is boiled up with a little water, which is presently decanted, and this operation is repeated until the liquid runs through, showing no alkaline reaction to litmus-paper. The whole of the precipitate is then transferred to the filter, which is then washed once or twice with the wash-bottle. A few drops of the liquid are collected on a strip of clean glass or on a watch-glass and evaporated to dryness. If the filtrate leaves no residue on evaporation the filter may be dried. When dry the precipitate is transferred to a previously weighed porcelain crucible, the paper folded and burnt, and the ashes



placed in the crucible. It is better not to heat this precipitate longer than is necessary to completely burn the filter. After the final ignition the crucible and contents must be cooled in a desiccator and accurately weighed.

*Note.*—This method is only applicable to crystallised copper sulphate, or some such preparation, free from other metals capable of being precipitated by potash.

*Example.*—Copper sulphate—

	Grams.
Weighing tube with copper sulphate .	= 20·0640
After removal of sample for analysis .	= 18·1978

Copper sulphate taken for analysis = 1·8662

1st weighing—Weight of copper oxide + crucible + lid . . . . .	Grams.
	= 33·561

2d weighing after heating again to redness . = 33·561

Weight of crucible + lid . . . . . = 32·963

Weight of copper oxide + filter-ash . . . = 0·598

Weight of filter-ash . . . . . = 0·002

Actual weight of copper oxide = 0·596

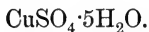
To find the percentage of copper oxide in 1·8662 grams of copper sulphate—

$$\frac{0·596 \times 100}{1·8662} \overset{\text{Per cent.}}{=} \underline{\underline{31·93 \text{ CuO}}}$$

The quantities may be stated thus—

	Found.	Calculated.
CuO	31·93	31·90 per cent.

## 11. ESTIMATION OF WATER IN CRYSTALLISED COPPER SULPHATE.



A pair of watch-glasses with ground edges are fitted together edge to edge, and kept closed by means of a wire clip. Each glass is marked No. 1, with a writing diamond near to the edge; the clip is also marked with a notch made by a file. The watch-glasses are opened and placed with the clip on a white tile, or piece of glazed paper in the water-oven and heated to 100° C. After fifteen or twenty minutes they are removed, closed by the clips, placed in a desiccator to cool, and subsequently weighed. Some of the crushed crystals are transferred from the weighing tube to one of the watch-glasses, the other is placed over it, the clip is fitted on, and they are weighed again. The glasses are then opened, and placed with the clip in the water-oven as before; heating is continued for an hour. The glasses are removed, closed, cooled in a desiccator and weighed. The operation is repeated until the weight is constant. The loss of weight represents water lost at 100° C., usually termed **water of crystallisation**. Should there be any diffi-

culty in obtaining a constant weight by heating in the water-oven, an air-bath should be used, the temperature of which is not allowed to rise much above  $105^{\circ}\text{C}$ . The glasses are now removed to an air-bath, and, proceeding as before, the weight is recorded after the substance has been heated to higher temperatures until no further loss of weight can be noted. Of course great care must be exercised lest in the manipulation any, even the smallest portion, of solid substance is spilled, as the results would thus be vitiated. The loss of weight at temperatures higher than  $100^{\circ}\text{C}$ . represents **water of constitution**. The following are a series of numbers obtained in the manner described :—

(1.) Weight of watch-glasses + clip (No. 1) +	Grams.
copper sulphate . . . . .	= 18.6476
Weight of watch-glasses + clip (No. 1)	= 17.2175
<hr/>	
Weight of copper sulphate taken for	
analysis . . . . .	= 1.4301
<hr/>	
(2.) Weight of watch-glasses and salt after	
drying at $100^{\circ}\text{C}$ . . . . .	= 18.238
<hr/>	
Weight of watch-glasses + salt (1)	= 18.6476
Weight of watch-glasses + salt (2)	= 18.2380
<hr/>	
Loss of weight after drying at $100^{\circ} = \text{H}_2\text{O}$	= 0.4096
<hr/>	

After drying at  $110^{\circ}$  C. for half an hour—

(3.)	Weight of watch-glasses + salt	.	.	.	= 18.2285
(4.)	After drying at $200^{\circ}$ C.	.	.	.	= 18.2200
(5.)	„ „ $210^{\circ}$ C.	.	.	.	= 18.215
(6.)	„ „ $210^{\circ}$ C.	.	.	.	= 18.2045
(7.)	„ „ $230^{\circ}$ C.	.	.	.	= 18.181
(8.)	„ „ $240^{\circ}$ C.	.	.	.	= 18.130
(9.)	„ „ $240^{\circ}$ C.	.	.	.	= 18.129
	Final weighing	.	.	.	= 18.129

(2.)	Weight of watch-glasses + salt dried at $100^{\circ}$	= 18.2380
(9.)	Weight of watch-glasses + salt dried at $240^{\circ}$	= 18.1290

Loss of weight between $100^{\circ}$ and $240^{\circ}$	
= $\text{H}_2\text{O}$	= 0.1090

The results may be thus stated—

	Grams.	Per cent.
Copper sulphate taken for analysis	= 1.4301	...
Water expelled at $100^{\circ}$	= 0.4096	28.64
„ „ $240^{\circ}$	= 0.109	7.62

$$\frac{.4096 \times 100}{1.4301} = 28.64 \text{ H}_2\text{O. Per cent.}$$

$$\frac{.109 \times 100}{1.4301} = 7.62 \text{ H}_2\text{O.}$$

	Found.	Calculated for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .
Water of crystallisation	= 28·64	28·8 per cent.
Water expelled at 240° C.	= 7·62	7·2 „
	<u>          </u>	<u>          </u>
Total water in crystals	= 36·26	36·0 „
	<u>          </u>	<u>          </u>

Previous examples **9** and **10** have given us numbers for sulphuric acid reckoned as  $\text{SO}_3$ , and for copper oxide,  $\text{CuO}$ . We may thus state the composition of crystallised copper sulphate and compare it with that calculated from the formula usually assigned to it. The percentage of course should add up to 100, but it is not often that such perfect accuracy is attained.

#### COMPOSITION OF CRYSTALLISED COPPER SULPHATE.

	Found.	Calculated for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .
$\text{CuO}$ . . .	= 31·93	31·9 per cent.
$\text{SO}_3$ . . .	= 32·02	32·1 „
$\text{H}_2\text{O}$ (at 100°) .	= 28·64	28·8 „
$\text{H}_2\text{O}$ (at 240°) .	= 7·62	7·2 „
	<u>          </u>	<u>          </u>
Total	= 100·21	100·0
	<u>          </u>	<u>          </u>

It is evident that the slight inaccuracy occurs in the determination of the water at temperatures above 100° C.

## 12. ESTIMATION OF CARBONIC ACID IN CARBONATES.

Soda ash. Sodium carbonate,  $\text{Na}_2\text{CO}_3$ . Soda crystals,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . Calcite,  $\text{CaCO}_3$ . Strontianite,  $\text{SrCO}_3$ . Witherite,  $\text{BaCO}_3$ . Magnesite,  $\text{MgCO}_3$ . Siderite,  $\text{FeCO}_3$ . Cerusite,  $\text{PbCO}_3$ . Dolomite, marble, limestone.

The process consists in liberating the carbonic acid from the substance by acting upon a weighed quantity by means of an acid which forms a soluble salt with the




FIG 5.

base. Carbon dioxide escapes as a gas, and the operation being conducted in a weighed flask the amount of gas escaping is estimated by the loss of weight observed. A flask is fitted up like Fig. 5; its capacity may be 100 c.c. to 200 c.c., or thereabouts. The flask and fittings should be as light as possible.

Take two test-tubes about 3 to 4 inches in length; one of these is to be drawn out at its closed end to a tube  $\frac{1}{4}$  of an inch in diameter, with an opening from which the gas may escape. The second tube is cut in two by scratching it all round with a sharp file  $1\frac{1}{2}$  to 2 inches from its closed end, and then touching the mark with a piece of very hot glass rod heated to

melting in the blow-pipe flame. A slight lip may be made on the tube with a conical piece of charcoal when the glass has been softened in the flame. The tube is to be suspended in the flask by means of a thread of silk or a horsehair. Two daffy corks, thoroughly sound and free from cracks, are then squeezed so as to soften them. In default of a proper cork squeezer, this may be done by wrapping them each in paper and rolling them on the floor beneath the sole of the foot. These corks are neatly bored, coated with, or soaked in melted paraffin, and tightly fitted with quill-glass tube of about  $\frac{1}{8}$  of an inch in diameter. The large cork for the flask is bored for two holes, that for the calcium chloride tube for one. The tube descending to the bottom of the flask is straight and open at each end; the edges are rounded by being softened in a gas flame. It projects above the cork 1 to 2 inches.

The exit tube just passes through the cork; it is bent first at right angles, then in the shape of a narrow : the ends of this tube must be rounded. The calcium chloride tube, loosely plugged at the narrow end with a piece of cotton wool, is filled up with half-fused porous calcium chloride. It is best fitted for absorbing moisture when broken into fragments about the size of swan-shot or small peas, and sifted so as to separate dust. At the wide end the tube is again loosely plugged with cotton wool, and then closed with

a perforated cork and the bent tube. This fitting must be tested to ascertain if air passes quite freely by placing a piece of black india-rubber tube over the narrow end, and sucking. It should require no effort to draw air through; otherwise it must be unpacked, and the cotton wool plugs must be loosened. Stoppers may be provided for the ends of the two tubes by taking two small corks, say  $\frac{1}{4}$  of an inch in diameter, and  $\frac{1}{2}$  an inch in length, and boring holes half-way through them, so that they fit tightly over the ends of the tubes; or bits of india-rubber may be stretched over pieces of glass tube sealed at one end, and then fitted on to the tubes.

The small test-tube is next removed from the flask and suspended by a loop on the thread or horse-hair from the hook on the balance, its weight is taken, and there is introduced 0.5 to 1 gram of the mineral; it is weighed again. Into the flask are introduced about 20 c.c. of strong hydrochloric acid mixed with an equal volume of water. The tube containing the mineral is slung inside the flask by the thread, so that it is inclined at about  $45^\circ$ , the cork is inserted, the stoppers to the tubes are removed, and the flask and contents are weighed. After the exact weight has been recorded, the flask is inclined to allow of a drop or two of acid to act on the carbonate; when effervescence has ceased the flask is inclined again, and the operation is repeated until all the mineral has been dissolved and the contents



of the tube washed out into the body of the flask. The gas evolved is charged with minute particles of liquid carried upwards as the bubbles burst, and also with the vapour of the liquid; the former particles are stopped by the cotton wool, and the vapour is retained by the calcium chloride, so that the gas escapes in a dry state. The apparatus, however, retains carbonic acid in solution in the liquid, and to remove this when all effervescence has ceased the flask should be gently warmed on the top of a water-oven, if such a thing is at hand, or on wire gauze, or a hot iron plate. A piece of india-rubber tube is then attached to the calcium chloride tube, the stopper is removed from the straight tube, and air is gently drawn through the flask by applying the lips to the tube, to withdraw all the carbon dioxide with which the flask is filled, for this being heavier than air would add to the apparent weight of the flask. The apparatus is then allowed to cool, and weighed again; the loss of weight is that of the carbon dioxide expelled from the mineral.

	Grams.
Weight of mineral taken . . .	= 1.4705
Weight of apparatus charged . . .	= 96.3665
Weight of apparatus after the disengagement of $\text{CO}_2$ . . .	= 95.7185
Loss = weight of $\text{CO}_2$	= 0.6480

Calculation to find the percentage of carbon dioxide in the mineral—

$$\frac{.648 \times 100}{1.4705} = \underline{\underline{44.0 \text{ CO}_2}} \text{ Per cent.}$$

*Notes.*—(1.) Should it be desired to operate upon a mineral containing lead such as cerusite, or upon white lead, nitric must be substituted for hydrochloric acid.

(2.) It is better to remove the stoppers from the tubes before weighing.

(3.) The corks are steeped in paraffin to prevent their absorption of moisture.

### 13. ESTIMATION OF CARBON DIOXIDE IN CARBONATES—LIMESTONE.

**Another Method.**—A platinum crucible or capsule, provided with a cover of platinum foil, is first heated to redness over a Bunsen burner for five minutes and transferred to a desiccator to cool. Weigh the crucible, and transfer to it 0.5 gram of the finely powdered limestone, and determine its weight accurately. Now ascertain the amount of moisture present by passing a Bunsen flame under the crucible so as to heat it very strongly for five minutes, but not to redness, cool in a desiccator, and weigh. Repeat the operation until the

weight is constant. The loss represents moisture. The limestone in the crucible is next mixed with 2 grams of previously fused and vitrified borax reduced to powder; the mixing is effected by stirring with a rounded glass rod or with a stout wire, the stirrer being wiped with some of the powdered borax placed on a sheet of paper, which is afterwards added to the borax in the crucible. Weigh the crucible and contents again. The mixture should be heated over a Bunsen burner for twenty minutes, then raised to a full redness over a blast-lamp or blow-pipe for another twenty minutes, or until there is no further escape of carbon dioxide, and a clear glass remains. The crucible is then cooled under a desiccator and weighed.

*Example.*—Limestone—

	Grams.
Weight of platinum capsule and cover . . . . .	= 9.850
Weight of limestone . . . . .	= 0.602
<hr/>	
Weight of limestone, capsule, and cover . . . . .	= 10.452
<hr/>	
Weight of borax, limestone, capsule, and cover . . . . .	= 12.887
Weight of borax, limestone, capsule, and cover after fusion . . . . .	= 12.601
<hr/>	
Weight of CO <sub>2</sub> . . . . .	= 0.286
<hr/>	

$$\frac{0.286 \times 100}{0.602} = 47.5 \text{ CO}_2 \text{ Per cent.}$$

Three results with two limestones, A and B, obtained by six experimenters—

A.		B.	
CO <sub>2</sub>		CO <sub>2</sub>	
47·5	} per cent.	39·6	} per cent.
47·6		39·1	
47·5		39·6	

*Note.*—All volatile matter, such as water or bituminous matter, must first be expelled from the limestone by heating to a temperature short of redness.

#### 14. ESTIMATION OF LIME.

Marble, Calcite, CaCO<sub>3</sub>.

Weigh out about 1 gram of the finely powdered substance into a flask of about 250 c.c. capacity, moisten the powder with water, and add dilute hydrochloric acid in small quantities, in order that the effervescence may not be too violent. When the action has moderated add some more acid, and if solution proceeds slowly, warm the liquid until all decomposition of the carbonate has ceased. There should be no solid residue, but if any insoluble particles remain the solution must be filtered, the flask rinsed out with about 10 c.c. of water three times on to the filter, the filter washed completely with a stream of hot water from the washing bottle. The

filtered liquid must be mixed with ammonium chloride to retain any magnesia in solution and ammonia in excess. There should be no precipitate; but if any forms, the liquid must be boiled and the precipitate filtered off. The liquid is thus freed from oxide of iron and alumina.

A little more ammonia is added, and ammonium oxalate is poured into the beaker as long as any precipitate falls. In this way calcium oxalate is precipitated while magnesia is retained in solution by the ammonium chloride. The mixture is boiled, the precipitate allowed to settle, the liquid decanted and filtered. The precipitate is washed twice by decantation with hot distilled water, transferred to the filter and washed with small quantities of hot water, each of which should run through the filter before the next is added. This is continued until the washings give no turbidity if about 5 c.c. are collected in a test-tube and tested with calcium chloride. The precipitate is dried in the water-oven or in a current of warm air, and ignited in a porcelain or platinum crucible just previously weighed.

Burn the filter in the manner described on p. 17. The crucible is then fitted into a hole made in a piece of asbestos cardboard, which is supported on a tripod and tilted up at one side. The lid of the crucible is removed and heat is cautiously applied to the crucible, the material within is seen to shrink and gradually be-

come grey. The heat may then be increased to the greatest intensity of a blast-lamp, and maintained for half an hour. The first process of ignition converts the calcium oxalate into carbonate, and the higher temperature changes the carbonate into caustic lime. The lid is then placed on the crucible, which is allowed to cool in a desiccator, and the contents are afterwards weighed as CaO. Repeat the heating and weigh again until a constant weight is attained.

*Example.*—Dolomite—

	Grams.
Weighing-tube + dolomite, before .	= 30·8155
Weighing-tube + dolomite, after .	= 29·3472
	<hr/>
Dolomite taken for analysis	= 1·4683

The mineral was dissolved cautiously in hydrochloric acid, the solution evaporated to dryness and dissolved in water acidified with hydrochloric acid. An insoluble residue was filtered off, which amounted to 2·4 per cent. The percentage of lime was found as follows:—

	Grams.
Crucible + lid + CaO .	= 38·781
Crucible + lid .	= 38·230
	<hr/>
	0·551
Filter-ash . . .	= 0·006
	<hr/>
Weight of CaO	= 0·545

To find the percentage of CaO in 1.4683 parts of dolomite—

$$\frac{0.545 \times 100}{1.4683} = 37.1 \text{ per cent.}$$

## 15. ESTIMATION OF MAGNESIA.

Epsom salts,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . Kieserite,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ .

Magnesite,  $\text{MgCO}_3$ . Dolomite.

The hydrated minerals must be crushed to powder and dried by pressure between folds of blotting-paper. The powder is then transferred to a well corked test-tube.

Weigh out from 0.5 to 1 gram of the substance, dissolve it in 50 c.c. to 100 c.c. water, or by the aid of hydrochloric acid if insoluble in water. Filter the solution if turbid or if anything remains undissolved, and collect the filtrate in a beaker capable of holding between 300 and 400 c.c. of liquid. Add to the clear solution from 25 to 40 c.c. of ammonium chloride and an excess of ammonia, so that the liquid smells strongly ammoniacal. Cautiously add, while stirring, a solution of sodium orthophosphate until no further precipitation occurs. Stir the liquid well, but without allowing the stirring rod to touch the sides of the beaker. Allow the mixture to stand covered over for twenty-four hours, decant the clear liquid on to

a filter, wash the precipitate with distilled water to which some ammonia has been added, decant the washings on to the filter by a stream of dilute ammonia directed from a wash bottle into the beaker, the mouth of which has a glass rod held across it, so that the liquid runs down the rod into the funnel without splashing. Some of the precipitate is sure to adhere to the beaker; this may be removed by washing with ammoniacal water, and at the same time rubbing with the feather end of a quill, or, what is better, with a glass rod, the end of which has an inch or so of black india-rubber stretched over it. When the whole of the precipitate has been transferred to the filter, wash with a few drops of ammoniacal water, and test the filtrate with silver nitrate, and a subsequent addition of nitric acid. As soon as the liquid shows no trace of phosphate or chloride of silver under these circumstances, the filter may be dried. When dry, the precipitate must be transferred to a porcelain or platinum crucible in the manner already described. The filter must be burnt on platinum wire, and the ash added to that in the crucible. It is more difficult to burn all the carbon off the filter with this precipitate than with others; and should this difficulty occur, a drop of fuming nitric acid may be let fall from the end of a glass rod, or from a very small pipette, on to the ash when the crucible is very hot; or, just before drying, the difficulty may be obviated by saturating the



filter with a very strong solution of ammonium nitrate, and burning the filter in a porcelain crucible, after the precipitate has been transferred thereto. In this way the ash is almost entirely consumed. The precipitate is then strongly ignited over the blow-pipe for twenty minutes, or until the residue is quite white. The crucible is cooled in a desiccator and weighed, the contents being magnesium pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ .

*Notes.*—(1.) The ammonio-magnesium-phosphate is slightly soluble in water, but not in dilute ammonia; hence the washing is performed with the latter.

(2.) When using a platinum crucible it is necessary not to add the filter to the crucible until it has been burnt on a platinum wire, since it is very difficult otherwise to burn off all the carbon. Moreover, there is a danger of the phosphate being reduced to magnesium phosphate, which would corrode the crucible.

(3.) Though in many cases a porcelain crucible may be used, without much disadvantage, in place of one of platinum, yet, in this instance, the much higher temperature to which the precipitate may be heated over the blow-pipe without risk of breakage, and the consequently more complete combustion of the filter-ash in a given time, render it advantageous to use platinum.

*Example.*—A specimen of dolomite was dissolved in hydrochloric acid and filtered from insoluble matter, evaporated to dryness, dissolved in water, and again filtered; the calcium was precipitated as oxalate, and the liquid was filtered. Ammonium chloride had already been added, the liquid was then made strongly ammoniacal, and the magnesia precipitated in the manner described.

	Grams.
Weight of dolomite + weighing-tube, before	= 32.1750
Weight of dolomite + weighing-tube, after .	= 30.8155

$$\text{Dolomite taken for analysis} = \underline{\underline{1.3595}}$$

Weight of crucible + lid + $\text{Mg}_2\text{P}_2\text{O}_7$	. = 38.7641
Weight of crucible . . . . .	= 38.2300

Weight of $\text{Mg}_2\text{P}_2\text{O}_7$ + filter-ash	. . = 0.5341
Weight of filter-ash . . . . .	= 0.0060

$$\text{Weight of } \text{Mg}_2\text{P}_2\text{O}_7 = \underline{\underline{0.5281}}$$

$\text{Mg}_2\text{P}_2\text{O}_7 = 222$  parts, contain  $2\text{MgO} = 80$  parts, thus—

$\text{Mg}_2$	$24 \times 2 = 48$	$\text{Mg}_2 = 48$
$\text{P}_2$	$31 \times 2 = 62$	
$\text{O}_7$	$16 \times 7 = 112$	$\text{O}_2 = 32$
	222	80
	222	80

To find the quantity of magnesia in 0.5281 parts of magnesium pyrophosphate—

$$\frac{80 \times 0.5281}{222} = 0.1903 \text{ MgO.}$$

To find the percentage of MgO in 1.3595 parts of dolomite—

$$\frac{0.1903 \times 100}{1.3595} = 14 \text{ per cent nearly, or, more precisely, } 13.997 \text{ per cent.}$$

## 16. LIMESTONE, DOLOMITE.

**Estimation of Lime, Magnesia, Ferric Oxide, Alumina, Carbon Dioxide, Silica, and Moisture.** Powder about 10 grams of the mineral.

**Estimation of Moisture.**—Weigh out 2 to 2.5 grams of the powdered mineral in a small evaporating basin or crucible, and dry it in the air-bath, on a plate of iron, or on a piece of asbestos cardboard, heated by a Bunsen burner, weigh it at intervals of about ten to twenty minutes until it ceases to lose weight. Cool in a desiccator before each weighing.

**Estimation of Carbon Dioxide.**—This is to be carried out according to the method of solution given in **Example 12**. If necessary, it may be confirmed by ignition with anhydrous borax, as in **13**.

**Estimation of Sand and Clay.**—The solution in hydrochloric acid contained in the flask after the evolution of carbon dioxide has ceased, and the apparatus been weighed, is filtered into a porcelain basin sufficiently large to hold the liquid and washings of the filter. The residue on the filter is thoroughly washed with hot water until no longer acid to test-paper; the paper is removed from the funnel, folded, placed in a previously weighed crucible, and heat applied, gently at first until the paper is dry. The temperature is then raised to redness until all the paper has been consumed. The residue is weighed and described as **sand and clay**.

In the event of the limestone containing much organic matter, weigh it on a previously dried and weighed filter (p. 19), and when the weight is constant at 100° C., ignite and proceed as already described.

**Estimation of Combined Silica.**—The acid solution and washings from the siliceous residue are mixed with a little nitric acid, evaporated to dryness, and the residue digested with hydrochloric acid till nothing remains undissolved but white flakes of silica. Should the evaporation be difficult to carry to dryness, a little water may be added two or three times, and evaporation continued on the water-bath, or over a flat burner, with a number of very small flames—the flames being placed at least 6 inches below the bottom of the basin. The

soluble matter is then treated with water and a little hydrochloric acid, boiled and filtered hot. The silica collected on the filter is washed until the washings are no longer acid, carefully dried, the silica transferred to a previously weighed crucible, and the paper burnt on a platinum wire. A strong ignition is then cautiously applied until the paper is consumed completely. Care should be exercised that the silica, which is very light when heated, is not carried away by currents of air. It is best at first to cover the crucible. The silica is weighed as  $\text{SiO}_2$ .

#### **Estimation of the Ferric Oxide and Alumina.—**

The acid solution from the silica is mixed with a considerable quantity of ammonium chloride and an excess of ammonia, and gently heated; the precipitated ferric hydrate and alumina is filtered off, washed until the washings yield no precipitate with silver nitrate, dried, ignited, and weighed as  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ . The limestone may contain the iron as ferrous carbonate, in which case an inaccuracy creeps in here if the quantity is more than trifling. If there is much iron, this must be separated from the alumina, and calculated as  $\text{FeO}$ .

**Separation of Iron and Alumina.**—Proceed as follows:—After the precipitation with ammonia and complete washing, the precipitate, if large in amount, is treated on the filter with hydrochloric acid, the liquid is allowed to flow into a silver dish (or a dish of pure

nickel); a hole is then made in the apex of the filter by passing a glass rod through it, and all traces of the precipitate are washed into the dish. The filter is then again moistened with acid, and thoroughly washed with water. A concentrated solution of perfectly pure caustic potash or soda, free from iron, alumina, and silica, is added to the filtered liquid in large excess and boiled. The precipitate formed is filtered off, washed thoroughly with boiling water, redissolved in hydrochloric acid, and reprecipitated by adding an excess of ammonia and subsequent heating. The precipitate is filtered, washed with hot water, dried, ignited, and weighed as  $\text{Fe}_2\text{O}_3$ . It is calculated as  $\text{FeO}$ .

**Estimation of Alumina.**—The solution in caustic alkali is acidified with dilute hydrochloric acid, boiled, and treated with a slight excess of ammonia; a drop of ammonium sulphide may be added. It is filtered, washed completely, dried, ignited, and weighed as  $\text{Al}_2\text{O}_3$ .

**Estimation of Lime.**—The filtrate from the precipitate of iron and alumina must be mixed with an excess of ammonium oxalate until no further precipitate falls. The magnesia remains in solution. The liquid is boiled and filtered. The precipitate is washed thoroughly until silver nitrate no longer yields a precipitate with the washings, dried, transferred to a previously weighed crucible, the filter burnt separately, and the crucible gently ignited. During ignition the calcium oxalate is

converted into carbonate. At a red-heat the calcium carbonate is partially decomposed into caustic lime. Moisten the powder when cool with a drop or two of water, and test with a very minute fragment of red litmus or turmeric paper; if there be any alkaline reaction add a little powdered ammonium carbonate to the crucible and a drop of water. Heat on the water-bath till dry. Now remove the crucible, and place it on a triangle as if for ignition; take a Bunsen burner, and, holding it in the hand, move the flame beneath the crucible so that it is heated strongly enough to volatilise the ammonium carbonate, but not sufficiently to become red-hot and render the lime caustic; weigh, heat again, and ascertain if the weight is constant; if not, repeat the addition of water and ammonium carbonate. Weigh as  $\text{CaCO}_3$ .

**Estimation of Magnesia.**—This is to be made in the filtrate from the calcium oxalate, according to 15.

*Example*—Dolomite.—The insoluble residue of this specimen contained a little carbon. Without giving the details which have been already given in several of the preceding examples, the results are as follows:—Moisture was not estimated. Of sand and clay there was none. Alkalies were not estimated—

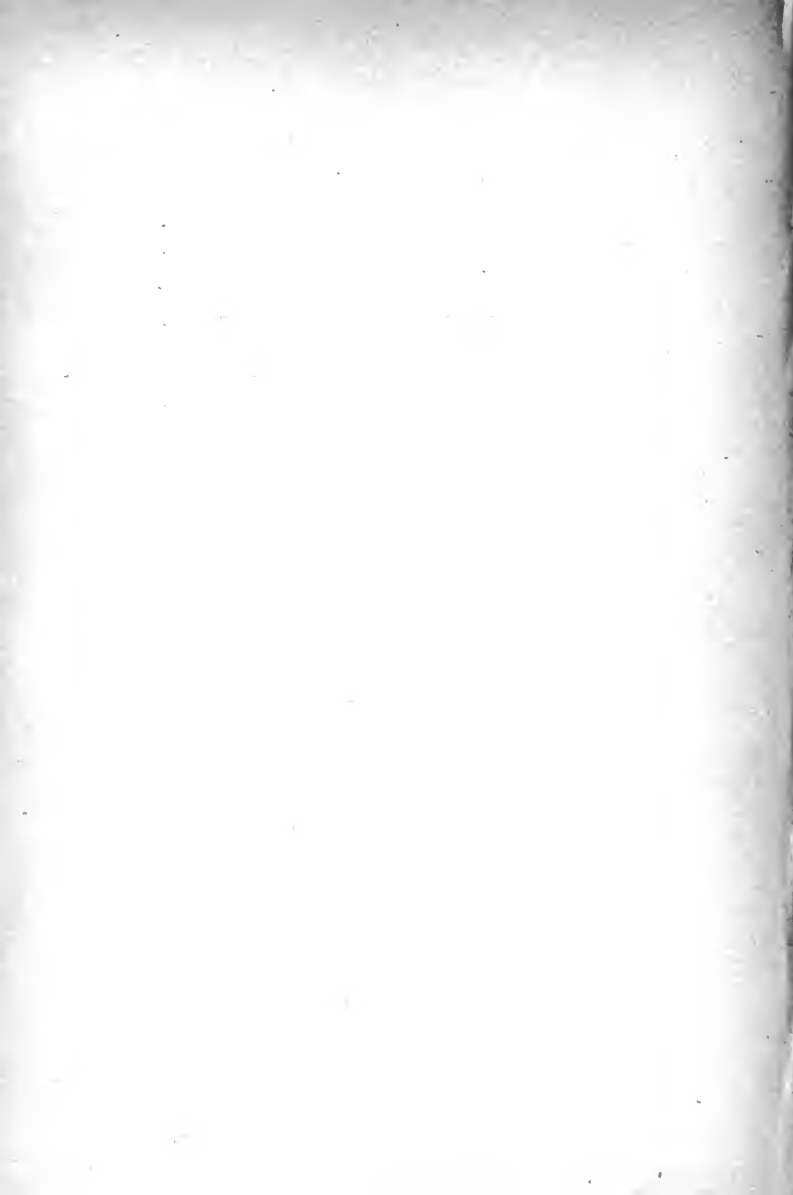
	er cent.
Carbon dioxide . . .	44·0
Silica . . .	2·2
Ferric oxide . . .	2·0
Lime . . .	37·3
Magnesia . . .	13·99
	<hr/>
	99·49
	<hr/>

**Estimation of Alkalies in Limestone.**—Dissolve 20 grams of the powdered mineral in hydrochloric acid, add a few drops of nitric acid, boil, and then add ammonia and ammonium carbonate in excess. Allow the liquid to stand over-night, filter, wash, evaporate the filtrate to dryness in a platinum basin, and ignite the residue to remove the ammonium salts. The residue is now dissolved in water, and boiled with a little milk of lime to precipitate bases other than the alkalies. Remove the insoluble matter by filtration, and wash. The excess of lime is removed from the filtrate and washings by the addition of ammonium carbonate and then ammonium oxalate. Filter off the precipitated calcium carbonate and oxalate, evaporate to dryness, and ignite again. Take up the residue with a very small quantity of water, and, if necessary, pass the solution through a small filter, then acidulate with hydrochloric acid, and evaporate to dryness in a platinum dish which has been previously weighed. Weigh and

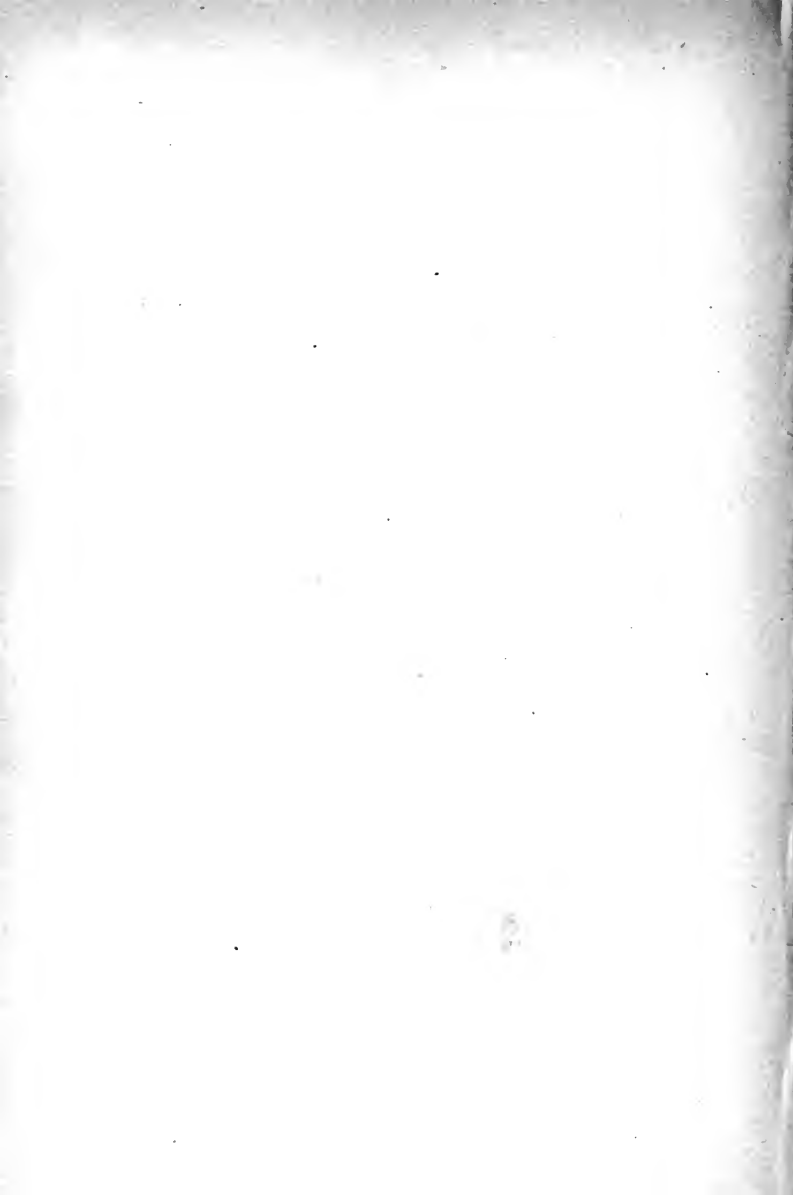


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dry the dish and its contents until the weight is constant. Subtract the weight of the dish, and thus is obtained the weight of the alkalies as chlorides. By estimating the amount of chlorine present by means of silver nitrate (see 8 or 28, pp. 47 and 115), the bases as oxides may be calculated, since 71 parts of chlorine are equivalent to 16 of oxygen.



METHODS OF VOLUMETRIC  
AND  
TECHNICAL ANALYSIS



## VOLUMETRIC ANALYSIS

## INTRODUCTION.

If molecular proportions of any two reagents are dissolved in separate portions of water and made up to equal volumes, a measure of the one will exactly react with an equal measure of the other, and a little more or less will become an excess or a deficiency of the reagent in the mixed solutions. When the solutions have been thoroughly mixed, all that we require is some delicate test which, while it will not interfere with the reaction, will indicate the presence of an excess of one or other of the reagents.

The molecular weight of sodium carbonate,  $\text{Na}_2\text{CO}_3$  is 106, and that of sulphuric acid is 98. These substances react in accordance with the equation—



If, therefore, in 1 litre of a solution there are 106 grams of sodium carbonate, every cubic centimetre of this will exactly neutralise 0·098 gram of sulphuric acid according to the following table :—

Solution.	Sodium Carbonate.		Sulphuric Acid.	
		Grams.		Grams.
1000	c.c. containing	106	neutralise	98
100	c.c. „	10·6	„	9·8
10	c.c. „	1·06	„	·98
1	c.c. „	·106	„	·098
0·1	c.c. „	·0106	„	·0098

If 100 c.c. of a solution, which makes a drop of litmus solution turn red, require 35 c.c. of sodium carbonate to be added before a purple tint is obtained, then the quantity of free acid in 100 c.c. of this liquid is represented by— $0.0098 \times 35 \text{ c.c.} = 0.343 \text{ gram}$ , or nearly 0.343 per cent. If 100 grams of the acid be weighed instead of simply measured, this percentage will be exact.

Solutions used in volumetric analysis are called **standard solutions** or **normal solutions**. A standard solution may be of any arbitrary strength according to some fixed standard, which is found more convenient for one reason or another than any other strength; as, for instance, a solution of silver nitrate of such a strength that 1 c.c. will precipitate 1 milligram of chlorine.

A normal solution is one in which 1 c.c. of the solution exactly reacts with a quantity of another substance equivalent to 1 milligram of hydrogen. Thus 23 is both the **atomic weight** and **equivalent weight** of sodium, and therefore 1 c.c. of a normal solution of sodium carbonate is made to contain 23 milligrams of sodium or 53 milligrams of sodium carbonate, not 106 milligrams, which is the molecular proportion.

Sometimes it is desirable that a normal solution should contain an atomic proportion, as, for instance, in the case of iron, or such a quantity of a reagent as will react with an atom of iron.

It is distinctly to be understood that wherever **parts** are mentioned, this means parts by weight, and **volumes** mean measures or parts by bulk.

The instruments used are very simple, consisting of **measuring flasks** for large quantities of liquid, **test mixers**, **pipettes** marked to deliver known volumes of solutions, and **burettes** or tubes, which have a scale engraved upon the glass by which the quantity of a standard solution used may be read off.

The most convenient form of burette is that of Geissler, which is a long tube with a lateral glass spigot upon it. The commonest form is Mohr's burette, a tube

with the lower end constricted; upon this a piece of india-rubber tube of small dimensions is tied. The india-rubber is pinched by a brass spring, which prevents the liquid flowing out by a glass nozzle terminating the tube, except when it is held open by the fingers. This is generally called a pinch-cock.

Standard solutions, which are generally prepared at

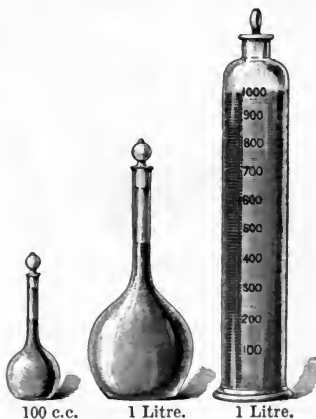


FIG. 6.—Measuring Flasks and Test Mixer.

15° C., should be used at that temperature as nearly as possible, or they may be standardised again immediately before use at any other temperature. An error amounting to two-tenths of a per cent may be introduced by the expansion of a solution when warmed to 25° C. When changes of temperature so considerable are unavoidable, greater accuracy may be secured by weighing instead of simply measuring the solution.

## ALKALIMETRY AND ACIDIMETRY.

### 17. PREPARATION OF A NORMAL SOLUTION OF SODIUM CARBONATE.

To prepare a normal solution of sodium carbonate it is necessary to dissolve an equivalent weight of the compound in a litre of water. For this purpose the salt must be perfectly free from any impurity. As ordinary sodium carbonate contains both chloride and sulphate, and the commercial bicarbonate, though much purer, is not free from these impurities, it is found best to prepare the pure carbonate specially for the purpose.

**The Preparation of Pure Sodium Carbonate.**—A considerable quantity, say a pound, of ordinary commercial “bicarbonate of soda” ( $\text{NaHCO}_3$ ) is powdered thoroughly and thrown into an equal bulk of cold water, the mixture is stirred, allowed to stand, and then

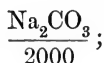


decanted. The operation is repeated. The mass is then thrown on to a large filter and drained thoroughly. It is then drenched with water, drained again, and the process is repeated twice. The last portion of washings which drain away are tested for sulphate and chloride. A second washing will frequently remove the sulphate, but a fourth is required to separate all the chloride. The process depends upon the small proportion of sulphate and chloride present, and the readier solubility of these salts than of the acid sodium carbonate. There is considerable loss of material owing to the wash water being a saturated solution of the salt. The pure carbonate is then drained on a porous tile, in a perforated funnel, or between folds of blotting-paper. It is dried at a temperature of about 120° C. and powdered. By this treatment the normal carbonate is produced according to the equation—



**Preparation of the Normal Solution.**—A portion of the dry salt is ignited in a porcelain crucible or in a small evaporating dish. The dish and contents are cooled in a desiccator and then weighed. Heating, cooling, and weighing are repeated until the weight is found to be constant, a quantity of the salt equal to half its molecular weight in grams is then dissolved in water and made up to 1 litre of solution in a marked flask.

The litre would then contain 53 grams of the carbonate, or 23 grams of sodium, equivalent to 1 gram of hydrogen. Each cubic centimetre of this solution would contain 23 milligrams of sodium. Such a solution may be represented by the formula—



since the molecule is diffused through 2000 parts of water, where Na = 23, C = 12, and O = 16 ;  $\text{Na}_2\text{CO}_3 = 106$ , and  $\frac{106}{2} = 53$ , the equivalent weight representing an atom of sodium or 23 parts.

Instead of taking an equivalent weight and a litre of water, 26 grams, or half an equivalent, and half a litre of water, may be found to be sufficient.

Generally speaking, it is more convenient when dealing with small quantities of material to proceed as follows :—The porcelain crucible or dish containing the ignited salt is weighed, and a small quantity, about 10 or 20 grams, is transferred to a dry beaker of not less than 250 c.c. capacity, and the requisite quantity of water is added to a saturated solution of the salt so as to bring its strength down to 53 grams per litre.

The volume which the solution should occupy is calculated thus—

Let  $w$  = the weight of sodium carbonate, and  $V$  = the volume of the normal solution in cubic centimetres,

then 
$$\frac{w (1000 \text{ c.c.})}{53} = V,$$

or 
$$V = \frac{w 1000}{53}.$$

Thus—

*Example.*—Weight of sodium carbonate taken = 9.703 grams ;

then 
$$\frac{9.703 \times 1000}{53} = 183.1 \text{ c.c.}$$

The weighed quantity of salt in the beaker-glass is dissolved by pouring upon it about 20 c.c. to 50 c.c. of boiling water, this is transferred without losing a drop of the liquid to a small test mixer, the flask is then rinsed three or four times by a stream of cold water from a wash bottle, and the rinsings are added to the liquid in the test mixer ; subsequently, when all the solution has thus been removed from the beaker, water is added to bring the volume up to 180 c.c., and 3.1 c.c. are run in from a burette. The solution is then well shaken, so as to mix it thoroughly.

*Notes.*—(1.) In adding water to make up a certain volume, it is almost impossible to keep the flow from an ordinary tap or from a washing bottle under proper control, so that there is great risk

of adding too much. It is found advantageous to add the last portions from a small beaker, or a test-tube, or better, from a dropping-tube, kept for the purpose.

- (2.) White jugs which can be washed and dried by wiping the inside with a linen cloth are very useful for mixing solutions. Liquids can be stirred in them with strips of glass an inch-or-two wide. Ordinary white basins of a quart capacity, with strips of glass as stirrers, are useful for titration, when the liquid has not to be heated.

## 18. THE PREPARATION OF NORMAL NITRIC ACID.

Ascertain the strength of pure nitric acid by finding its specific gravity with a hydrometer at 60° F. or 15° C. (see p. 236), and referring to tables giving the percentage of real acid. Find the quantity of real acid in each cubic centimetre of the reagent. Calculate the number of cubic centimetres of the reagent, which must be diluted to a litre in order to yield a solution of

the strength  $\frac{\text{HNO}_3}{1000}$ ,  $\frac{63}{1000}$ , or 63 grams of nitric acid in

1000 c.c. of solution, which is conveniently denoted by this formula.

*Example.*—The temperature being  $15.3^{\circ}\text{C.}$ ; sp. gr. of acid, 1.41; strength of acid, 69 per cent: hence 1 c.c., weighing 1.418 grams, contains

$$\frac{1.418 \times 69}{100} = 0.978 \text{ gram real acid.}$$

Where  $\text{H} = 1$ ,  $\text{N} = 14$ , and  $\text{O} = 16$ ,  $\text{HNO}_3 = 63$ , and the normal acid contains

$$\frac{\text{HNO}_3}{1000} \text{ or } \frac{63}{1000}.$$

Since 1 c.c. contains 0.978 gram real acid, the volume of this acid required in a litre of normal acid will be

$$\frac{63}{0.978} = 64.4 \text{ c.c.}$$

Hence 64.4 c.c. of the acid may be delivered out of a burette into a litre flask, and then diluted up to the mark. The acid is mixed completely by being poured out into a large dry jug or beaker and stirred well with a slip of glass an inch-or-two broad.

## 19. TITRATION OF A NORMAL ACID BY SODIUM CARBONATE.

**Preparation of an Indicator of Acidity.**—Before operating with the normal solutions it is well to become familiar with the changes of colour which are caused by

acids and alkalies in a dilute solution of litmus. If tincture or infusion of litmus be blue, it should be very carefully rendered neutral by the addition of a very dilute nitric acid, drop by drop, until, after shaking, a violet tint remains. If the liquid is strongly blue, it should be made brilliant red by means of nitric acid, and very dilute alkali (caustic soda or caustic potash) should be added, until a violet colour results. A few drops of the neutral litmus should then be dropped into a pint beaker and half-filled with distilled water. Note the addition of 0.1 c.c. of nitric acid; also, in like manner, observe the action of 0.1 c.c. of sodium carbonate solution. Boil the liquid, and add one more drop, 0.1 c.c. of the carbonate. Remark how the liberated carbonic acid causes the litmus to become of a wine-red colour, which, after boiling, becomes permanently blue if the alkali is in slight excess. Other indicators may be used instead of litmus, such as helianthin or methyl-orange, fluoresceine, phenol-pt haleine, and aurine, provided their sensitiveness is first tested. Helianthin is to be preferred; it is an orange-coloured salt which becomes purple on the addition of an acid. Tinge about 100 c.c. of distilled water with the litmus solution of exactly the neutral violet tint, and keep this in a beaker on a sheet of white paper for comparison.

**Titration of the Soda Solution.**—Measure out 50 c.c. of the normal soda solution in a marked 50 c.c.

flask, or with a 50 c.c. pipette, or run the requisite quantity into a beaker of about 200 c.c. capacity. Add a few drops of litmus and warm the liquid. For this purpose the beaker should be placed on wire gauze over a gas-burner. Add from a burette about 45 c.c. of normal nitric acid. When effervescence has ceased, boil. Further additions of acid are to be made cautiously, and the liquid is boiled briskly after each addition. Finally, the acid is added drop by drop, until, after boiling, a permanent reddish violet tint, indicating neutrality, is attained by the liquid. Not fewer than three titrations should be made with different portions of the alkaline solution. The burette should be read after each titration, and the quantity used should be noted at the time, the readings being exact to  $\frac{1}{10}$  of a cubic centimetre.

*Example.*—Quantity of sodium carbonate used: (1) 50 c.c.; (2) 50 c.c.; (3) 50 c.c.

Acid required: (1) 49.9 c.c.; (2) 50 c.c.; (3) 50 c.c.

This acid is strictly normal.

That is to say—1 c.c. containing half a molecule  $\frac{\text{Na}_2\text{CO}_3}{2}$

or .053 gram of sodium carbonate, will neutralise

$\text{HNO}_3$  or .063 gram nitric acid.

$\text{HCl}$  or .0365 gram hydrochloric acid.

$\frac{\text{H}_2\text{SO}_4}{2}$  or .049 gram sulphuric acid.

## 20. THE STANDARDISING OF ACIDS BY MEANS OF SODIUM.

When pure sodium carbonate is not obtainable, proceed in the following manner :—

A block of sodium is cleansed from naphtha by pressure between folds of filter-paper, and cut rapidly with a large cork-knife, so that each surface is but very little tarnished, giving the metal a purplish or bluish tint. The piece of metal, which, if possible, should not be touched with the fingers, is instantly placed in a capsule, such as may be made out of two test-tubes by cutting off their lips and inverting one within the other. When the tubes fit properly, sodium can be weighed in them quite accurately.

When no blocks of sodium are at hand, but only small pieces, put sufficient of them into a test-tube, *quite dry of course*, and cover with paraffin oil. Heat until the sodium melts into a bright globule. Allow to cool, pour off the paraffin, wrap the sodium in blotting-paper, and then wipe with a dry, clean, linen cloth ; weigh as before.

The sodium is dissolved in 50 to 100 c.c. of pure alcohol, in a flask of 350 c.c. capacity, the neck of which is inclined, a stream of water running over the body of the flask to cool it. When the sodium ethylate becomes viscid and the action slow, a drop of water may be added,



and this effects the solution of the metal quietly and completely. If a deci-normal solution of alkali be desired, it is only necessary to make up the liquid to the required volume. If, however, a simple titration to fix the strength of an acid is wanted, dilute with an equal bulk or more of water, and proceed as usual.

*Example—*

	Grams of Sodium.	Acid c.c.	$H_2SO_4$ in 1000.
(1)	0.620 required	25.8	= 51.20 grams.
(2)	0.713     ,,	29.7	= 51.13     ,,
(3)	0.742     ,,	30.7	= 51.42     ,,
		Mean = 51.25	,,

The pieces of sodium were weighed in a capsule and dropped one after the other into three flasks containing alcohol, the weight of each piece of sodium being of course known by difference in four successive weighings.

Two precipitations with barium chloride of 25 c.c. of the acid gave in each case 3.041 grams  $BaSO_4$ , indicating 51.2 parts  $H_2SO_4$  per 1000.

## 21. ESTIMATION OF $H_2SO_4$ IN OIL OF VITRIOL.

Weigh out about 30 grams of oil of vitriol in a beaker provided with a watch-glass cover. The beaker and its cover are previously weighed. Transfer the acid to a

flask of 500 c.c. capacity, avoiding loss. Rinse out the beaker three or four times with cold water, and pour the rinsings into the flask. Dilute the acid with about 300 c.c. of water, cover the flask with an inverted beaker-glass, large enough to pass well over the mouth of the flask, and place the flask with its cover under the tap, so that water may flow over to cool it. When the liquid is quite cold, fill up to the 500 c.c. mark with cold water.

Three separate titrations with 50 c.c. of the sulphuric acid are to be made with the solution of normal sodium carbonate.

*Example—*

Weight of oil of vitriol 34·89 grams, diluted to 500 c.c.

	Acid taken.	Sodium Carbonate required.
(1)	50 c.c.	66·2 c.c.
(2)	50 c.c.	66 c.c.
(3)	50 c.c.	66 c.c.

As 1 c.c. of sodium carbonate solution is equivalent to 0·049 gram of sulphuric acid,  $0·049 \text{ gram} \times 66 = 3·234$  grams of sulphuric acid contained in 50 c.c. of the dilute acid titrated; but there were 34·89 grams of oil of vitriol diluted to 500 c.c. Therefore

$$\frac{32·34 \times 100}{34·89} = 97·72.$$

There are 97·72 per cent of sulphuric acid in the oil of vitriol.

## 22. THE ESTIMATION OF AMMONIA IN AMMONIUM SALTS.

When ammonium salts of powerful acids are heated with a solution of caustic alkali the ammonia is expelled. The alkali which has expelled the ammonia exists in the solution as a neutral salt; any excess that has been added remains caustic, and may be estimated by means of a standard acid.

Take 10 grams of ammonium chloride, preferably the pure crystallised salt, heat at  $100^{\circ}\text{C}$ . until its weight is constant. A porcelain crucible may be used for containing the salt. About 1 gram of the salt is transferred to a flask of about  $\frac{1}{2}$  litre capacity, containing 50 c.c. of water; the crucible with the salt is then weighed again, and the difference between the first and second weighings gives the weight of the salt taken.

Prepare a solution of caustic soda and titrate it with a normal sulphuric acid, then make up the solution to such a volume that 50 c.c. will exactly neutralise 50 c.c. of the acid.

To the solution of the ammonium chloride add from a pipette 50 c.c. of the caustic alkali, and boil vigorously till the steam no longer tinges turmeric-paper brown. Add to the liquid a few drops of a solution of helianthin, and titrate with normal acid until the yellow

colour changes to purple. Each cubic centimetre of the alkali which has lost its causticity is equivalent to 17 milligrams of ammonia.

*Example.*—Let  $m$  = number of c.c. of acid used, then  $50 \text{ c.c.} - m = n$ , the c.c. of alkali utilised in expelling the ammonia.

As the acid is normal, each c.c. = 0.017 gram of ammonia, or  $\text{NH}_3$ ;

therefore  $n (0.017 \text{ gram}) = x$ , the quantity of ammonia in the ammonium salt taken.

## VARIOUS VOLUMETRIC METHODS.

### 23. THE ASSAY OF IRON.

When potassium dichromate is added to a solution of a ferrous salt in presence of a free acid, the following reaction occurs: —  $6\text{FeSO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + 7\text{H}_2\text{SO}_4 = 3\text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O}$ .

From this equation it will be perceived that a molecule of the salt  $\text{K}_2\text{Cr}_2\text{O}_7$  is capable of oxidising  $6\text{FeSO}_4$ . For every atom of iron, therefore,  $\frac{1}{6}$  of a molecule of potassium dichromate is required. The molecular weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  is 294.8.

$$\text{K} = 39, \text{Cr} = 52.4, \text{O} = 16,$$

$$\text{and} \quad \frac{294.8}{6} = 49.15.$$

49.15 parts of potassium dichromate, or  $\frac{1}{6}$  of a molecule, in 1000 c.c. constitute a normal solution, and each c.c. is equivalent to 0.056 gram of iron. It is found that a solution  $\frac{1}{10}$  of this strength gives more accurate results.

**Preparation of a Deci-normal Solution.**—Well crystallised potassium dichromate is gently fused by heating in a porcelain crucible. The fused mass is crystalline and free from water. It is removed from the crucible, crushed and powdered. About 5 grams of the salt are weighed out into a beaker, dissolved in a minimum of water, and then made up to such a volume that there are 4.915 grams in 1000 c.c.

Let  $w$  = the weight of salt taken,

then  $\frac{w \text{ 1000 c.c.}}{4.915}$  is the volume to which the solution must be diluted.

*Example.*—Weight of salt taken, 9.246 grams,

then  $\frac{9.246 \times 1000 \text{ c.c.}}{4.915} = 1881 \text{ c.c.}$ , the volume of the

deci-normal solution.

The solution was made at first in about 30 c.c. of water transferred to a litre flask, and the beaker rinsed three or four times very carefully with water, the rinsings were poured into the flask, then the flask was filled up to the mark. This solution was poured into a large

vessel capable of holding two litres, and into the litre flask there were poured carefully measured quantities of 500 c.c., 250 c.c., 100 c.c., and 33 c.c. of water, which were afterwards added to the solution in the bottle, making in all 1881 c.c.

**Titration of the Dichromate Solution.**—It is necessary to prepare a solution of pure iron of known strength. This may be done by selecting well-formed crystals of ammonium ferrous sulphate; the formula of the salt is  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ . The crystals, which should be dry, but not effloresced, are crushed to powder and pressed between blotting-paper to remove any moisture which may have been enclosed in the crystals. A porcelain crucible, with lid, is weighed, and a small quantity of the salt is weighed in it. One-seventh the weight of the salt represents metallic iron. A convenient quantity to take for each titration is about 1.5 gram; it may be dissolved in 50 c.c. of water, acidulated with 50 c.c. of sulphuric acid of approximately normal strength—that is to say, one volume of oil of vitriol mixed with twenty volumes of water.

Instead of using a ferrous salt, which is not always at hand, or procurable in a perfectly pure state, fine “flower wire,” or annealed iron wire, will answer the purpose. The wire must be bright; if necessary, it may be cleaned with fine emery cloth. About 0.2 gram of the wire is weighed out and doubled up, or cut into pieces with

scissors, and introduced into a flask of about 100 c.c. to 150 c.c. capacity. Fifty cubic centimetres of dilute sulphuric acid are placed in the flask, which is then covered with a watch-glass, and warmed until the whole of the metal has dissolved; the solution must be used immediately, since the ferrous sulphate is liable to be oxidised by the entrance of air into the flask. The air may be excluded by fitting the flask with a perforated cork, through which passes a quill tube, 2 inches in length. Slipped over the tube and outside the flask is a piece of black india-rubber tubing, with a longitudinal slit in it  $\frac{1}{2}$  an inch long (Fig. 7). Above the slit the tube is closed at the end with a stopper of glass rod. The slit in the rubber acts as a valve, through which the hydrogen may escape; when the atmosphere of the flask contracts upon cooling, the excess of pressure without closes the slit so that air cannot enter. Before attempting to remove the cork, slip off the india-rubber, or remove the stopper of glass rod to allow the air to enter. The flask containing the solution of iron is emptied into a beaker, and rinsed out with water which has been boiled, to expel air. The decinormal solution of dichromate is added to the ferrous sulphate, and, after each addition, stirred with a glass rod. The reduction of the chromate to chromium



FIG. 7.

sulphate is made evident by the yellow solution becoming green. The termination of the reaction, however, cannot be observed in this way, but is recognised by the fact that, while potassium ferricyanide strikes a deep blue colour with a ferrous salt, this reaction ceases as soon as complete oxidisation has been effected. A crystal of potassium ferricyanide is washed with water, dried with a cloth, and then dissolved in about 40 parts of cold water. A white plate is spotted with small drops of this solution taken up with a glass rod. After each addition of the dichromate solution the glass rod is withdrawn and a drop of the liquid allowed to fall on to a drop of the ferricyanide ; the blue colour, at first strong, becomes faint, and when the reaction ceases the analysis is finished. It is necessary to make the last additions of the solution very cautiously, about two drops at a time.

*Example.*—0.245 gram of pianoforte wire are weighed. The true weight of the iron in this may be reckoned as 99.7 per cent, or  $0.245 \text{ gram} \times 0.997 = 0.2442 \text{ gram}$ . There were 44.4 c.c. of deci-normal solution of potassium dichromate required, therefore

$$1 \text{ c.c.} = \frac{0.2442}{44.4}$$

$$= 0.0055 \text{ gram of iron.}$$



## 24. ESTIMATION OF IRON IN IRON ORES.

The ores, which may be examined in the manner about to be described, are **magnetite**,  $\text{Fe}_3\text{O}_4$ ; **red hæmatite**,  $\text{Fe}_2\text{O}_3$ ; **brown hæmatite**,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ; **siderite**,  $\text{FeCO}_3$ ; and other ores containing the ferrous carbonate, such as **black-band** and **clay iron-stone**.

**The Sampling of Ores.**—Ores to be analysed for commercial purposes must be first very carefully sampled. Differences between two analyses may often be traced to bad sampling; therefore, to expend time and labour on the analysis of material which does not represent the average quality of the ore is worse than useless, because it is misleading. Several pieces of the ore should be taken from the different parts of a large heap; these should be coarsely powdered and mixed, and about half a pound should be taken from the bulk and preserved in a well-stoppered bottle for analysis. A convenient quantity may be still more finely powdered, and one-half of this is reduced to a very fine powder in an agate mortar, sifted through very fine gauze, and again powdered until it no longer feels gritty between the fingers.

**The Estimation of Iron.**—Five grams of the finely powdered ore are introduced into a flask of about 250 c.c. capacity, together with 10 c.c. of water,

and 30 c.c. of strong hydrochloric acid: the mixture is gently heated and occasionally agitated until all effervescence caused by the decomposition of carbonates has ceased; the temperature is then raised and the mixture boiled for about fifteen minutes. The solution of the iron is then reduced by one of two methods from the state of perchloride to that of protochloride. (1) Sulphuretted hydrogen may be passed through the liquid contained in a flask until it is quite colourless and charged with the gas, when it must be boiled until all excess is expelled. The steam issuing from the mouth of the flask should be tested from time to time with paper dipped in a solution of lead acetate until it no longer causes a brown stain. (2) It may be reduced by zinc; for this purpose, pieces of the pure metal about the size of small beans are put into the flask to the quantity of 50 or 100 grams, and the liquid is boiled, a cork and india-rubber valve being fitted to the flask (Fig. 7). The liquid may then be rapidly filtered into a 250 c.c. flask and made up to the requisite volume with previously boiled and cooled water. For each titration 50 c.c. or 100 c.c. are taken, according to the quantity of potassium dichromate required, the liquid being removed with a pipette. Thus 50 c.c. may be added to the first, and a second titration commenced, almost the whole of the requisite quantity of the volumetric solution being added at once. The operation is then repeated in the

same way. The indicator used is, as before, potassium ferricyanide.

The quantity of ore is 5 grams in 250 c.c.; 50 c.c. =  $\frac{1}{5}$ , and therefore each titration is performed upon 1 gram. Supposing that the following quantities of solution have been used:—

$$\left. \begin{array}{l} (1) 50.2 \text{ c.c.} \\ (2) 49.8 \text{ c.c.} \\ (3) 50 \text{ c.c.} \\ (4) 50 \text{ c.c.} \end{array} \right\} \text{Mean, 50 c.c.}$$

Then we may assume that 50 c.c. are required for each gram of ore, and as the solution is of such a strength that 1 c.c. = 0.0055 gram of iron,  $50 \times 0.0055 = 0.275$  grams, there are 0.275 gram of iron in 1 gram of ore, or 27.5 in 100 grams., *i.e.* 27.5 per cent.

Ores, however, frequently contain both ferrous and ferric compounds, and in order to determine the quantity of each a series of titrations is made first with the ferric compounds unreduced, and secondly after reduction has taken place. This will, of course, require double the quantity of material to be operated upon. It is usual, then, to reckon the iron as protoxide and peroxide by deducting the iron found, in the first instance, from that found in the second, and calculating their corresponding weights in ferrous and ferric oxides. Where Fe = 56 and O = 16, corresponding weights of iron, fer-

rous oxide, and ferric oxide, are represented by the numbers 56, 72, and 80, since

$$2\text{Fe} = 56 \times 2 = 112 \qquad \frac{112}{2} = 56$$

$$2\text{FeO} = 56 \times 2 + 16 \times 2 = 144 \qquad \frac{144}{2} = 72$$

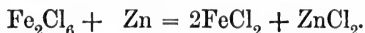
$$\text{Fe}_2\text{O}_3 = 56 \times 2 + 16 \times 3 = 160 \qquad \frac{160}{2} = 80.$$

Hence a solution which is deci-normal may be used for estimating iron, ferrous oxide, or ferric oxide, by substituting for the factor 0.0056 for iron, 0.0072 for ferrous oxide, and 0.008 for ferric oxide.

If the solution is not strictly deci-normal, but contains 0.0055 gram of iron instead of 0.0056 gram, then

$$\begin{aligned} 1 \text{ c.c.} &= \frac{0.0072 \times 0.0055}{0.0056} \\ &= 0.00707 \text{ gram of ferrous oxide.} \end{aligned}$$

*Note.*—The reduction process is of much importance in the estimation of iron. The reactions are the following :—



## 25. THE DETERMINATION OF IODINE BY SODIUM THIOSULPHATE.

### **Preparation of a Deci-normal Solution of Iodine.**

—For this purpose it is necessary to obtain purer iodine than that which can be purchased. Commercial re-sublimed iodine is intimately mixed with about one-fourth its weight of pure potassium iodide and placed on a large watch-glass or a dial-glass. Two other glasses of the same size are then accurately weighed, and one of them is placed over that containing the iodine. If the edges of the glasses are not ground so as to fit accurately, they may be fixed together by means of gummed paper. It must be observed that the upper glass should not come in contact with the mixture of iodine and potassium iodide, but there should be a fair space between the two. When the glasses have been properly adjusted they may be heated on an iron dish, but not strongly. Pure iodine sublimes and condenses upon the upper watch-glass in brilliant crystalline plates. When the operation is finished, the upper watch-glass is removed and inverted, the clean watch-glass which was weighed with it being used as a cover, the pair are placed under a desiccator, cooled and weighed. The increase in weight gives the amount of pure iodine condensed. By this process chlorine and bromine, which

the iodine in the crude state may contain, are retained as potassium salts, equivalent quantities of iodine being of course liberated.

The atomic weight of iodine being taken as 126.5, a deci-normal solution will contain 12.65 grams per litre.

Let  $w$  = the weight of iodine taken, and  $V$  the volume of a deci-normal solution containing  $w$ , then—

$$V = \frac{w(1000 \text{ c.c.})}{12.65}$$

	Grams.
<i>Example.</i> —Weight of watch-glasses + iodine	= 12.2312
Weight of watch-glasses . . . . .	= 10.8862
	<hr/>
Iodine	= 1.345
	<hr/> <hr/>

$$\frac{1.345 \times 1000 \text{ c.c.}}{12.65} = 106.3 \text{ c.c.}$$

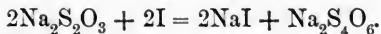
The watch-glasses containing the iodine were put into a beaker of water with 1.8 to 2 grams of pure potassium iodide dissolved in about 21 c.c. of water, which is poured over them in order to dissolve the iodine. The solution was transferred to a 100 c.c. flask, the beaker and contents rinsed three times with 20 c.c. of water, the watch-glasses removed and rinsed, and the rinsings added to the flask, which was then filled up to the mark. Subsequently 6.3 c.c. of water were added from a burette.

The solution was then transferred to a beaker, and well stirred with a strip of glass so as to mix it thoroughly.

**The Preparation of Starch as an Indicator.**

—2 or 3 grams of starch are roughly weighed and rubbed into a thin paste with water in a mortar. About 250 c.c. of water are boiled in a beaker, and the starch liquid is poured into the boiling water little by little, and stirred after each addition. The whole is then boiled for five or ten minutes and allowed to settle. The clear liquid is decanted from any sediment. Or heat 100 parts of concentrated glycerine with 6 parts of starch to 190° C. for about an hour, pour into water, and precipitate the soluble starch with alcohol, and filter. This preparation is kept as a thick paste, and for use a small quantity is taken out on the end of a glass rod.

**Preparation of Deci-normal Sodium Thiosulphate Solution.**—The composition of this salt is  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 248$  parts; a deci-normal solution therefore contains 24.8 grams per litre. Well crystallised sodium thiosulphate is powdered and dried by pressure between folds of blotting-paper. Of the powder 24.8 grams are dissolved in water and made up to a litre. When iodine reacts upon sodium thiosulphate, the following equation is realised—



The salt  $\text{Na}_2\text{S}_4\text{O}_6$  is sodium tetrathionate. As long

as this reaction occurs on the addition of the iodine solution, so long will the blue colour which the iodine gives to the starch paste be destroyed. In this case the indicator, or starch solution, is put into the liquor which is being titrated, so that the blue colour is communicated to the whole of the liquid. Immediately, therefore, that the whole of the thiosulphate is converted into tetrathionate, the least excess of iodine will act upon the starch, and the blue colour will be permanent.

*Example.*—A solution of thiosulphate prepared in the manner described was titrated with the iodine solution, a few drops of starch being put into the liquid. As the iodine solution flowed from the burette a blue colour appeared, and immediately vanished on agitating the liquid. After a time the disappearance of the colour became less rapid; violet tints were noticed to be formed, until a point was reached when a faint violet colour was imparted to the whole of the liquid, and the next drop of iodine established a permanent beautiful blue colour.

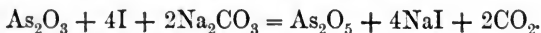
25 c.c. of thiosulphate solution in about 100 c.c. of water required (1) 24.9 c.c.; (2) 25 c.c.; and (3) 25 c.c. of iodine solution.

The solution was therefore deci-normal.



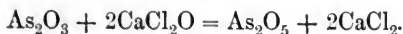
## 26. ESTIMATION OF CHLORINE AND ACTIVE OXYGEN, BY SODIUM ARSENITE.

**Preparation of a Deci-normal Solution.**—Pure sodium arsenite is prepared by dissolving 4.95 grams of the purest sublimed arsenic trioxide in about 250 c.c. of distilled water, to which are added 25 grams of pure crystallised sodium carbonate; this salt must be free from sulphide, sulphite, or thiosulphate. The arsenic trioxide must be in powder, and to bring it into solution it must be frequently agitated during ebullition. The liquid, when ready, is transferred to a litre flask, the original flask being rinsed repeatedly, the rinsings added to the bulk of the liquid and water filled up to the mark. In order to ascertain the strength of this solution, 10 c.c. are put into a beaker with a little starch solution, and a deci-normal solution of iodine is run in, when, in presence of water, the following reaction takes place:—



As soon as the pure iodine ceases to be converted into sodium iodide the excess strikes a blue colour with the starch. If 10 c.c. of the iodine are used for 10 c.c. of the arsenite it is strictly deci-normal.

With bleaching powder the reaction is as follows:—



It will be observed in both the above reactions, that  $\text{As}_2\text{O}_3 = 198$  parts react with  $4\text{Cl} = 142$  parts, and that  $\frac{198}{4} = 49.5$  parts of arsenic trioxide are capable of reacting with 35.5 parts of chlorine, or 1 atom, and therefore 4.95 with 3.55 of chlorine.

To make a solution of bleaching powder of such a strength that each c.c. of deci-normal sodium arsenite will indicate 1 per cent of chlorine, it is necessary to bear in mind that if 1 gram be taken, each c.c. of the standard solution used will indicate 0.00355 gram of available chlorine; but if  $0.00355 \times 100 = 0.355$  gram be taken, then each c.c. of the sodium arsenite will indicate 1 per cent of available chlorine.

## 27. BLEACHING POWDER.

**Estimation of Available Chlorine.**—Weigh 7.1 grams of the sample, previously well mixed, grind it with a little water in a porcelain mortar till a completely homogeneous thin paste has been obtained, dilute with more water, slightly grease the lip of the mortar on the outside, and then wash the whole contents into a litre flask, fill up to the mark, and take for each test 50 c.c. = 0.355 gram of bleaching powder, having shaken up the flask immediately before. Run into the above with continuous agitation an alkaline deci-normal solution

of sodium arsenite; then place a drop of the mixture on a piece of filter-paper, moistened with starch paste mixed with a solution of potassium iodide. If there is much chlorine a *brown* spot will appear, if less chlorine the spot will be *blue*. According to the depth of colour, more or less of the arsenite solution may be added. The test is repeated until there is scarcely any colour perceptible, or the colour is discharged altogether. The reaction is just finished when one drop of the solution completely destroys the last trace of colour. Each cubic centimetre of the arsenite solution indicates 1 per cent of available chlorine in the bleaching powder.

*Note.*—The atomic weight  $\text{Cl} = 35.5$  is always employed in commercial calculations.

## 28. ESTIMATION OF CHLORINE IN NEUTRAL SALTS.

This process is applicable to the estimation of chlorides, in potassium and sodium nitrates, in sea-water, and water used for domestic purposes. The chlorides are decomposed by silver nitrate, and complete precipitation is indicated by mixing a few drops of a solution of neutral potassium chromate with the solution to be tested. When silver nitrate is added to a solution of a chloride containing a neutral chromate, a red precipitate appears, which is silver chromate,  $\text{Ag}_2\text{CrO}_4$ , and this

immediately disappears on shaking, provided there is still some chloride unprecipitated. But when all the chloride is just completely precipitated, the slightest addition of silver nitrate will cause the formation of a deep red colour, which on agitation is diffused through the liquid, and communicates to it an orange tint. A solution of silver nitrate is made of such a strength that 1 c.c. = 0.001 gram of chlorine. The necessary quantity of silver nitrate for 1 litre is calculated in the following manner:—

Where  $\text{Ag} = 108$ ,  $\text{N} = 14$ , and  $\text{O}_3 = 48$ ,  $\text{Cl} = 35.4$  ;  
the molecular weight of  $\text{AgNO}_3 = 170$  ;

$$\text{hence } \frac{1000 \text{ c.c.} \times 0.001 \text{ gram} \times 170 \text{ grams}}{35.4 \text{ grams}} = 4.802 \text{ grams}$$

silver nitrate.

Powder some recrystallised silver nitrate and heat it in a porcelain crucible till fusion is about to take place. 4.802 grams of the salt are then dissolved in a litre flask, and water is added to make up the correct volume.

Some perfectly pure rock-salt is powdered and heated strongly in porcelain crucible till its weight is constant. A portion of this is weighed out and made up to 1 litre, so that 1 c.c. = 0.001 gram of chlorine, thus—

$$\begin{aligned} &\text{Where } \text{Na} = 23 \text{ and } \text{Cl} = 35.4 ; \\ &\text{the molecular weight of } \text{NaCl} = 58.4 ; \\ &\text{hence } \frac{1000 \text{ c.c.} \times 0.001 \text{ gram} \times 58.4 \text{ grams}}{35.4 \text{ grams}} = 1.6497, \text{ or} \end{aligned}$$

very nearly 1.65 gram sodium chloride.

Dissolve 1.65 grams of sodium chloride and make the solution up to 1 litre. The silver solution should then precipitate the chlorine from an equal volume of the salt solution.

Place 50 c.c. of the salt solution in a porcelain dish capable of holding 200 c.c., and add thereto two or three drops of a cold saturated solution of neutral potassium chromate. The salt should be tested to make sure that it is perfectly free from chloride. The silver solution is then added from a burette, the liquid being constantly stirred. The red colour at first formed disappears, but in time it disappears more slowly, and finally it remains permanent even after stirring. It may be remarked that when the quantity of chloride present is very small, as, for instance, in good potable waters, the last drop of silver nitrate causes the pale yellow colour to become not distinctly red, but of a slightly reddish shade, or merely of a *dull yellow*.

**To Determine Chlorine in Potable Waters.**—Measure 100 c.c. with a pipette into a porcelain basin, add a few drops of potassium chromate, and titrate with silver nitrate.

*Example—*

	The Vartry Water, Dublin.		Silver Nitrate.
(1)	100 c.c.	required	1.4 c.c.
(2)	100 c.c.	„	1.3 c.c.
(3)	100 c.c.	„	1.4 c.c.
		Mean	1.37 c.c.

There are 1.37 milligrams of chlorine per 100 c.c. of water, or 1.37 parts per 100,000 parts of the water.

When a solution of silver nitrate is kept for some time, a deposit forms and it becomes slightly weaker by a portion of the salt being decomposed. Under these circumstances it is necessary to determine its factor with a standard solution of sodium chloride, the operation being carried out in the manner already described. A solution of silver nitrate had originally been made of such a strength that 1 c.c. = 0.0005 gram of chlorine contained 2.401 grams per litre, as may be seen by the following calculation :—

$$\frac{1000 \text{ c.c.} \times 0.0005 \text{ gram} \times 170 \text{ grams}}{35.4 \text{ grams}} = 2.401 \text{ grams silver nitrate.}$$

The weight of sodium chloride which will react with 2.401 grams of silver nitrate is found thus—

$$\frac{58.4 \times 2.401}{170} = 0.8248 \text{ gram.}$$

Therefore 0.9772 gram of rock-salt was dissolved and made up to the volume of 1184 c.c.

$$\frac{0.9772 \times 1000}{0.8248} = 1184 \text{ c.c.}$$

25 c.c. of this solution should react with an equal volume of the silver nitrate if its strength is correct ;

but it was found by three experiments to be rather too weak, thus—

	Sodium Chloride.		Silver Nitrate.
(1)	25 c.c.	required	25·7 c.c.
(2)	25 c.c.	„	25·65 c.c.
(3)	25 c.c.	„	25·7 c.c.

The factor for the silver nitrate is therefore—

$$\frac{25}{25\cdot65} = \cdot9746 ;$$

that is to say, the number of cubic centimetres of the solution of silver nitrate used must be multiplied by the factor 0·9746.

The Dublin water was examined with this solution—

	Water required.	Silver Nitrate.
(1)	100 c.c.	2·9 c.c.
(2)	100 c.c.	2·7 c.c.
(3)	100 c.c.	2·8 c.c.

Mean 2·8 c.c.

Then  $2\cdot8 \text{ c.c.} \times \cdot9746 = 2\cdot729 \text{ c.c.}$

Chlorine.

But 1 c.c. of silver nitrate thus corrected = ·0005 gram.

2·729 c.c. „ „ = ·00136 gram.

If 100 c.c. therefore contain ·00136 gram chlorine, therefore 100,000 parts of water contain 1·36 parts of chlorine.

## 29. DETERMINATION OF THE HARDNESS OF WATER.

The hardness of water is measured by the quantity of soap which it is capable of destroying before it will form a permanent lather. If a solution of soap in weak alcohol is added drop by drop to 50 c.c. of distilled water, a certain quantity is required to form a good lather, but for every milligram of calcium carbonate contained in the water a further addition of soap is necessary.

**Preparation of a Standard Solution of Calcium Chloride.**—Weigh out 0.2 to 0.4 gram of pure calcium carbonate, such as fragments of calcite crystals, or finely crystalline white marble. Transfer the calcium carbonate to an evaporating dish of 4 inches diameter, or to a beaker-glass of half a pint capacity, containing 20 c.c. of dilute hydrochloric acid; cover the vessel with a glass plate to prevent loss by spurting, and digest on a water bath, with additions of fresh acid until all is dissolved. Evaporate to dryness on a sand-bath, or in an air-bath, or on a piece of asbestos cardboard; then add a little water and evaporate again, repeat this twice or thrice till hydrochloric acid ceases to evaporate from the salt, then dissolve in water and make up to such a strength that 1000 c.c. contain calcium equal to 0.2 gram of  $\text{CaCO}_3$ .



*Example.*—0.6076 gram of calcite was dissolved in hydrochloric acid and made up 3038 c.c.

$$\frac{.6076 \times 1000 \text{ c.c.}}{.2} = 3038 \text{ c.c.}$$

### **Preparation of a Standard Solution of Soap.—**

(a) A cake of Pears's transparent soap is scraped with a straight sharp edge of glass; 4 to 5 grams of the shavings are dissolved in 500 c.c. (or a pint) of proof spirit, or a mixture of two volumes of methylated spirit, with one volume of distilled water. (b) Or the above quantity of soap may be dissolved by heat in one volume of distilled water, and the two volumes of methylated spirit may be added subsequently. (c) A potash soap may be prepared by rubbing together in a mortar 15 grams of lead plaster (*Emplastrum plumbi*) and 4 grams of dry potassium carbonate. Add a little methylated spirit when the substances have become fairly well mixed, and continue rubbing until a creamy uniform mixture is obtained. Allow this material to stand for some hours, and then wash it on a filter repeatedly with methylated spirit.

Add half its volume of water to the soap solution, and then dilute a portion of it with a mixture of methylated spirit two volumes and water one volume, until 14.25 c.c. are required to form a permanent lather with 50 c.c. of the standard hard water prepared from calcium carbonate.

**Titration of the Soap Solution.**—Take 50 c.c. of the standard solution of calcium carbonate, 0·2 gram per litre, and transfer it by a pipette to a wide-mouth, stoppered bottle, capable of holding 100 c.c. The soap solution is added 1 c.c. at a time, the liquid being shaken violently after each addition, the stopper is removed and air sucked out of the bottle with a rather wide ( $\frac{1}{2}$ -inch) glass tube. At first a curd forms and no lather; after the curd has become abundant a lather commences to form, but the bubbles soon burst, and nothing but curd remains; at this stage the soap solution must be added with increased caution, and in smaller quantities at a time; and finally, when a lather remains without breaking for two minutes after shaking, when the bottle is lying on its side, the reaction is complete. With a very little practice it is easy to perceive when the conditions for forming a permanent lather are approached.

*Example.*—50 c.c. of the standard hard water required 10·35 c.c. of a soap solution; this is too strong, since it ought to have used up 14·25 c.c.; hence 103·5 c.c. were diluted with a mixture of two volumes of alcohol and one volume water up to a volume of 142·5 c.c., and this solution was found to be accurate.

**Determination of Hardness of Water.**—Hardness is described as temporary and permanent hardness, the former is destroyed by boiling, the latter is not. The difference between total hardness and permanent

hardness, or hardness remaining after the water has boiled, gives the temporary hardness.

**Total Hardness.**—Measure out 50 c.c. of the water with a pipette, place the stopper in the bottle and shake vigorously, draw off any carbon dioxide liberated by sucking air from the bottle with a glass tube. Proceed to titrate with the soap solution, adding not more than 2 c.c. at a time, shaking after each addition and extracting the carbon dioxide. Suppose that 16 c.c. of soap have been added, and that no permanent lather has been formed, then any further addition will not indicate the true hardness, because an undue proportion of alcohol is present. Take 10 c.c. of the water and dilute with distilled water up to 50 c.c. in a measured flask, transfer this to the bottle, proceed as before, and titrate; note the quantity of soap solution used and refer to the Table of Hardness, p. 125, which indicates the parts of calcium carbonate in 100,000 parts of water. The degree of hardness must then be multiplied by 5 in order to indicate the total hardness. The hardness must be reduced by dilution in order that no more than 16 c.c. of soap be used in forming a permanent lather, with 50 c.c. of water.

**Permanent Hardness.**—Take 200 c.c. of water, place in a flask, best of a conical shape, and boil hard for not less than fifteen minutes; cool the water, and make up its volume to 200 c.c. Transfer 50 c.c. of this

to the test bottle and titrate with soap solution. Note the number of c.c. used, and refer to the table for the corresponding degree of hardness.

*Example.*—50 c.c. of tap water were shaken up in the test bottle and the air was sucked out; 16 c.c. of soap solution were added by degrees without a sign of a permanent lather; 10 c.c. were then made up to 50 c.c. in a measured flask with distilled water recently boiled and cooled. The diluted water required in two trials—

- (1) 3·4 c.c. ;                      (2) 3·4 c.c. soap solution.

This corresponds to 3·77 parts of  $\text{CaCO}_3$  in 100,000 of water, and therefore the total hardness of the water was  $3\cdot77 \times 5 = 18\cdot85$  parts of  $\text{CaCO}_3$  in 100,000 parts of water.

50 c.c. of the water were boiled in a flask for fifteen minutes, filtered, made up to 50 c.c. with distilled water in a measured flask and titrated; 3·6 c.c. of soap solution were required to cause a permanent lather, which corresponds to a hardness of 4·03 parts of  $\text{CaCO}_3$  in 100,000 of water, hence—

	Parts $\text{CaCO}_3$ .	
Total hardness	= 18·85	} per 100,000 parts of water.
Permanent hardness .	= 4·03	
Temporary hardness .	= 14·82	

TABLE OF HARDNESS IN PARTS PER 100,000, 50 C.C.  
OF WATER BEING USED.

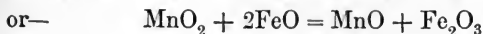
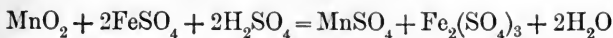
c.c. of Soap Solution.	CaCO <sub>3</sub> per 100,000.	c.c. of Soap Solution.	CaCO <sub>3</sub> per 100,000.	c.c. of Soap Solution.	CaCO <sub>3</sub> per 100,000.	c.c. of Soap Solution.	CaCO <sub>3</sub> per 100,000.	c.c. of Soap Solution.	CaCO <sub>3</sub> per 100,000.
·7	·00	3·8	4·29	6·9	8·71	10·0	13·31	13·1	18·17
·8	·16	·9	·43	7·0	·86	·1	·46	·2	·33
·9	·32	4·0	·57	·1	9·00	·2	·61	·3	·49
1·0	·48	·1	·71	·2	·14	·3	·76	·4	·65
·1	·63	·2	·86	·3	·29	·4	·91	·5	·81
·2	·79	·3	5·00	·4	·43	·5	14·06	·6	·97
·3	·95	·4	·14	·5	·57	·6	·21	·7	19·13
·4	1·11	·5	·29	·6	·71	·7	·37	·8	·29
·5	·27	·6	·43	·7	·86	·8	·52	·9	·44
·6	·43	·7	·57	·8	10·00	·9	·68	14·0	·60
·7	·56	·8	·71	·9	·15	11·0	·84	·1	·76
·8	·69	·9	·86	8·0	·30	·1	15·00	·2	·92
·9	·82	5·0	6·00	·1	·45	·2	·16	·3	20·08
2·0	·95	·1	·14	·2	·60	·3	·32	·4	·24
·1	2·08	·2	·29	·3	·75	·4	·48	·5	·40
·2	·21	·3	·43	·4	·90	·5	·63	·6	·56
·3	·34	·4	·57	·5	11·05	·6	·79	·7	·71
·4	·47	·5	·71	·6	·20	·7	·95	·8	·87
·5	·60	·6	·86	·7	·35	·8	16·11	·9	21·03
·6	·73	·7	7·00	·8	·50	·9	·27	15·0	·19
·7	·86	·8	·14	·9	·65	12·0	·43	·1	·35
·8	·99	·9	·29	9·0	·80	·1	·59	·2	·51
·9	3·12	6·0	·43	·1	·95	·2	·75	·3	·63
3·0	·25	·1	·57	·2	12·11	·3	·90	·4	·85
·1	·38	·2	·71	·3	·26	·4	17·06	·5	22·02
·2	·51	·3	·86	·4	·41	·5	·22	·6	·18
·3	·64	·4	8·00	·5	·56	·6	·38	·7	·35
·4	·77	·5	·14	·6	·71	·7	·54	·8	·52
·5	·90	·6	·29	·7	·86	·8	·70	·9	·69
·6	4·03	·7	·43	·8	13·01	·9	·86	16·0	·86
·7	·16	·8	·57	·9	·16	13·0	18·02	...	...

### 30. THE VALUATION OF MANGANESE ORES.

The ores of manganese are the minerals, **pyrolusite**,  $\text{MnO}_2$ ; **braunite**,  $\text{Mn}_3\text{O}_4$ ; **manganite** or **brown manganese ore**,  $\text{Mn}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ; **hausmannite**,  $\text{Mn}_3\text{O}_4$ ; and **wad**, of variable composition. The rules for sampling iron ores are to be observed in the case of manganese. The method of valuing manganese ores depends upon their power of oxidising a measured volume of a standard solution of a ferrous salt, and the estimation of the ferrous compound which remains in excess by means of a standard solution of potassium permanganate. The amount of iron indicated by the standard permanganate, deducted from the amount of iron used, gives the quantity of iron which has been oxidised by the manganese ore, and from this can be calculated the percentage of manganese dioxide or available oxygen contained in the ore.

The advantage of using permanganate for titrating the solution of iron is owing to the fact that a single drop of a standard solution will colour half a litre of water, and hence it requires no separate indicator.

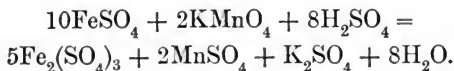
The reaction between manganic oxide and an acid solution of ferrous sulphate is as follows—



Hence—

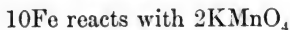
Manganic Oxide.		Oxygen.
Parts.		Parts.
87	=	16
10·875	=	2
1·0875	=	0·2

**Preparation of Standard Potassium Permanganate.**—When potassium permanganate is added to a solution of iron wire in sulphuric acid, or to a solution of ferrous sulphate acidified with sulphuric acid, the following reaction takes place :—



The molecular weight of potassium permanganate is 158 when  $\text{K} = 39$ ,  $\text{Mn} = 55$ ,  $\text{O} = 16$ .

According to the above equation,



hence 560 parts of iron react with 316 parts of permanganate containing 80 parts of active oxygen, and 28 parts of iron react with 4 parts of oxygen. A semi-normal solution of potassium permanganate containing 4 grams of oxygen per litre, available for oxidising 28

grams of iron, is made by dissolving  $316 \div 20 = 15.8$  grams of the crystallised pure salt in water, and making the volume up to 1 litre.

1 c.c. = 0.004 gram of oxygen.

### **Standardising the Permanganate Solution.—**

The available oxygen in the standard solution is estimated by means of the finest iron wire, which may be considered to contain 99.6 per cent of iron. Weigh out 0.5622 gram of pure iron wire, the amount equivalent to 0.56 gram of actual iron. Place it in the flask fitted with a cork and india-rubber valve (Fig. 7, p. 103), with 25 c.c. of dilute sulphuric acid, containing one-fifth of its volume of oil of vitriol; the solution of the wire may be hastened by warming. As soon as all the iron has dissolved, the solution is very carefully transferred to a wide-mouthed flask or to a beaker capable of holding a pint of liquid (500 or 600 c.c.) The flask is rinsed out several times with distilled water, and the rinsings are added to the solution, which is finally diluted with 250 c.c. of distilled water. Place the flask or beaker on a sheet of white paper or on a white plate, and add the permanganate cautiously from a burette with a lateral glass tap. After each addition the liquid must be agitated either by stirring with a glass rod, if a beaker be used, or by swirling the liquid round in the flask. Finally, it will be seen that the



liquid retains a permanent pink tint when a tenth of a cubic centimetre of permanganate has been added in excess of that necessary to completely oxidise the ferrous sulphate into a ferric salt. The colour should remain at least half a minute.

The quantity of iron taken should require exactly 20 c.c. of permanganate ; for each c.c. reacts with 0.028 gram of iron.

Suppose that the potassium permanganate is not quite pure, and that the solution is a little too weak, it is most convenient to find out the requisite quantity of the crystals to be added in order to make the solution strictly semi-normal.

Let  $m$  = the number of c.c. of the solution used,

$$\text{then} \quad \frac{\begin{array}{c} \text{Gram.} \\ 15.82 \times m \end{array}}{20} = \text{grams of solid perman-}$$

ganate to be added to 1 litre to produce an exactly semi-normal solution. The strength of the solution having been rectified, it is necessary to check it once more with iron wire.

It is sometimes convenient to weigh a quantity of permanganate crystals a little in excess of that required for a semi-normal standard, to find the exact strength of the solution with iron wire, and then to dilute it with the necessary amount of water.

The calculation would then take this form—

Let  $m$  = the number of c.c. used,

then  $\frac{m \times 1000 \text{ c.c.}}{20}$  = the volume in c.c. to which the

solution should be made up. Now it is to be observed that 100 c.c. of the semi-normal solution placed in a half-litre flask and filled up to the mark yields a deci-normal solution. It is more accurate, and therefore it is advisable to titrate the iron wire with this solution rather than with the stronger. Of course the quantity required for 0.56 gram of iron would be 100 c.c.

*Notes.*—(1.) Potassium permanganate cannot be kept in a bottle closed with a cork, neither can it be used with a Mohr's burette, the nozzle of which is fitted on with an india-rubber tube.

(2.) Instead of iron wire, the double sulphate of iron and ammonium may be used, which contains  $\frac{1}{7}$  its weight of iron,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ; or ordinary recrystallised ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; the crystals of either salt must be crushed and pressed between blotting-paper to remove moisture before being used, and kept in a stoppered bottle in a cool place.

**Estimation of Available Oxygen in Manganese Ore.**—It has been observed on p. 127 that 1.0875 grams of  $\text{MnO}_2$  are equivalent in oxidising power to 0.2 gram of oxygen, this being the quantity available for oxida-

tion in an acid solution. Weigh out 1.0875 grams of manganese ore, which has been ground as fine as possible and dried for some time at  $100^{\circ}\text{C}$ . Put it into the flask (p. 103) with the india-rubber valve and add 75 c.c. (in three pipettesful of 25 c.c. each) of a solution containing 100 grams pure crystallised ferrous sulphate and 100 c.c. pure concentrated sulphuric acid, diluted to 1 litre. The solution of ferrous sulphate should be standardised on the same day by means of the same 25 c.c. pipette, with a deci-normal solution of permanganate made by diluting that of semi-normal standard.

Close the flask, having tested the valve to see that it works properly, and heat until the manganese dioxide is completely dissolved, leaving possibly a light coloured residue. After complete cooling add 200 c.c. of water, and titrate with semi-normal potassium permanganate until a faint pink tinge remains. Deduct the quantity of permanganate now required from that corresponding to the 75 c.c. of iron solution; the remainder indicates for each cubic centimetre  $2(0.010875)$  gram, or 0.02175 gram = to 2 per cent of  $\text{MnO}_2$ .

**Estimation of the Hydrochloric Acid required for Decomposing Manganese Ore.**—The strength of the acid must first be ascertained with a normal solution of alkali; for this purpose 10 c.c. of ordinary strong hydrochloric acid are used.

Dissolve 1 gram of manganese ore in a flask, connected

with an inverted Liebig's condenser, and containing 10 c.c. of the hydrochloric acid. Warm the retort as much as may be necessary. Allow the solution to cool, and titrate with the normal alkali until reddish-brown flakes of ferric hydroxide appear, which remain insoluble after shaking. Deduct the standard alkali used for the ore solution from that originally employed in ascertaining the strength of the acid ; the corresponding quantity of acid will be that used in dissolving the manganese ore.

### 31. ESTIMATION OF PHOSPHORIC ACID.

This method depends upon the precipitation of ortho-phosphoric acid as uranyl phosphate,  $U_2P_2O_{11}$ , which is insoluble in acetic acid. The solution may contain free ortho-phosphoric acid or an acetic acid solution of an earthy phosphate. Should there be an excess of any other mineral acid present, it should be neutralised with an alkali and an alkaline acetate, after which an excess of acetic acid may be added.

The standard solutions required are—

- (a) Uranyl acetate,  $UO_2(C_2H_3O_2)_2 \cdot H_2O$ , or nitrate,  $UO_2(NO_3)_2 \cdot 6H_2O$ , 40 grams to the litre. If it be possible to procure the acetate it should be preferred.
- (b) Pure, recrystallised sodium ortho-phosphate,  $Na_2HPO_4 \cdot 12H_2O$ , crushed, and dried between

folds of filter-paper. The salts should show no signs of loss of water by efflorescence. Dissolve 10.085 grams and make up to 1 litre; 50 c.c. of this solution contain 0.1 gram  $P_2O_5$ .

- (c) Sodium acetate, 100 grams ; acetic acid, sp. gr. 1.04, 100 c.c.; water to the volume of 1 litre.

As an indicator, a freshly prepared solution of potassium ferrocyanide or freshly powdered crystals of the salt. Spots of the salt or solution on a white plate strike a brown colour, with a trace of the uranium nitrate or acetate. To check the strength of the solution of sodium ortho-phosphate take 50 c.c., evaporate to dryness in a platinum basin, and heat to redness. The sodium pyrophosphate should weigh 0.1874 gram.

Take 500 c.c. of the solution of sodium ortho-phosphate, and precipitate the phosphoric acid by addition of an excess of pure calcium chloride. Filter, wash away all traces of chloride, and dissolve the precipitate in a slight excess of nitric acid, make the volume of the solution up to 500 c.c. Place 50 c.c. of this solution in a weighed platinum basin or crucible, add a slight excess of ammonia, evaporate to dryness, ignite to expel the ammonium nitrate, cool in a desiccator, and weigh. The residue is  $Ca_3P_2O_8$ .

$Ca_3P_2O_8 = 310$ , represents  $P_2O_5 = 142$ : from these data the quantity of phosphoric anhydride in the solution may be calculated.

The solution may be further checked by adding a considerable excess of sodium acetate and acetic acid to 50 c.c. of the solution of the tricalcic phosphate, precipitating the phosphoric acid by uranyl acetate, and boiling well for some time. The liquid containing the precipitate is poured into a large beaker, filled up with boiling water, allowed to stand till quite clear, and the clear liquid removed with a syphon. The beaker is again filled with boiling water, and again removed when clear; this is repeated a third time, and then the precipitate is transferred to a filter; it requires very little subsequent washing. The precipitate cannot be filtered directly and washed on the filter on account of its bulky and slimy nature. Dry, ignite, and weigh as  $2(\text{UO}_3) \cdot \text{P}_2\text{O}_5$ .

$$2(\text{UO}_3) \cdot \text{P}_2\text{O}_5 = 718 ;$$

and

$$\text{P}_2\text{O}_5 = 142.$$

**Titration of the Standard Uranyl Acetate Solution.**—The strength of the calcium phosphate solution being known, it is diluted if too strong, so that 50 c.c. contain 0.1 gram of  $\text{P}_2\text{O}_5$ . Take 50 c.c. of the solution, add 5 c.c. of the sodic acetate solution, then heat and add about three-fourths of the calculated amount of the uranyl acetate solution; then proceed by testing frequently, say after each  $\frac{1}{2}$  c.c. has been added, until the first faint brown tinge appears. The quantity of the uranyl acetate used is taken as a guide to the

amount required. Take another 50 c.c. and proceed as before ; but add as far as can be ascertained the whole of the uranyl acetate at once, boil, and proceed cautiously, two drops or four drops at a time, until the last addition proves to be an excess. Repeat again carefully twice.

*Example.*—In 1 litre of  $\text{Ca}_3\text{P}_2\text{O}_8$  solution there were 2.21 grams  $\text{P}_2\text{O}_5$  ; 50 c.c. were taken, treated with ammonia or soda till alkaline, and then with acetic acid till strongly acid, after that with 5 c.c. of sodium acetate solution ; the solution was heated to  $80^\circ \text{C}$ ., and the uranyl acetate added with constant stirring. The liquid was tested by placing spots of a solution of potassium ferrocyanide on a porcelain plate and allowing a drop of the solution to fall upon each one, until the mixed drops become tinged with a reddish-brown colour. The beaker was warmed again and another drop of the liquid tested ; a drop of uranyl acetate was then added, and the colour being distinctly visible, no more of the solution was added.

50 c.c. required (1) 22.5 c.c. uranyl acetate.

”	”	22.6 c.c.	”
”	”	22.45 c.c.	”
”	”	22.5 c.c.	”

---

90.05 c.c.

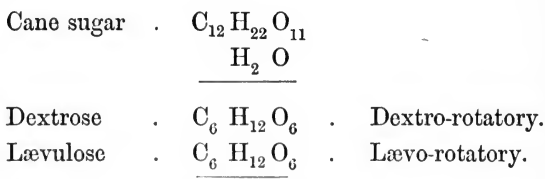
Mean      22.51 c.c.

## 32. THE ESTIMATION OF SUGAR.

Sugar is a name applied to various substances, of which there are two distinct groups, the most commonly occurring members of which are the following :—

I.	II.
<i>The saccharose, or cane-sugar group.</i>	<i>The glucose, or grape-sugar group.</i>
Formula.	Formula.
$C_{12}H_{22}O_{11}$	$C_6H_{12}O_6$
Saccharose or cane sugar.	Lævulose } Grape
Maltose or malt sugar.	Dextrose } sugar.
Milk sugar.	

By the addition of the elements of water to a molecule of a saccharose there result two molecules of glucose. Thus—



Cane sugar is converted half into dextrose and half into lævulose. When a solution of copper sulphate, potassium tartrate, and caustic soda, mixed in proper proportions, is boiled, the dark blue liquid undergoes no change ; but if only a very minute quantity of a glucose



or of maltose be present, then a slight warming causes the separation of a precipitate of cuprous oxide. The precipitate at first formed is cuprous hydrate, and this has a yellow colour; but on boiling it loses water, and becomes bright red.

One molecule of glucose exactly reduces 5 molecules of cupric oxide,  $\text{CuO}$ , to the state of cuprous oxide,  $\text{Cu}_2\text{O}$ .

Glucose.	
$\text{C}_6 = 72$	$\text{Cu} = 63.4$
$\text{H}_{12} = 12$	$\text{O} = 16.0$
	<hr/>
$\text{O}_6 = 96$	$79.4$
<hr/>	<hr/>
$180$	$79.4 \times 5 = 397$
<hr/>	

Hence 180 parts of glucose are capable of reducing 397 parts of cupric oxide. If the quantity of copper oxide reduced by a given solution of sugar is known, we may easily calculate from the above numbers the quantity of sugar present.

The method consists in adding the sugar solution to a definite quantity of a standard solution prepared from pure crystallised copper sulphate, mixed with potassium tartrate and caustic soda, until the deep blue colour has been destroyed.

**Preparation of the Standard Solution.—Fehling's Solution.**—34.64 grams of pure recrystallised copper sulphate, which has been powdered and pressed

between blotting-paper, are weighed out and dissolved in 200 c.c. of distilled water. In another vessel 173 grams of pure crystals of Rochelle salt, the double potassium sodium tartrate, are dissolved in 480 c.c. of a solution of caustic soda, sp. gr. 1.14. The two solutions are then mixed, and the clear blue liquid is poured into a litre flask, the vessels rinsed with distilled water two or three times, the rinsings added to the solution, and the flask filled up to the mark.

Each c.c. of this solution contains 0.3464 gram of copper sulphate, and represents exactly 0.05 gram of pure glucose.

The liquid should be put into small stoppered bottles, which are well filled and kept in the dark. If the stoppers do not fit properly the caustic soda will absorb carbonic acid, and a precipitate will occur when the solution is boiled. An addition of some freshly prepared caustic soda solution will prevent this.

As a rule it is best before titrating a solution of sugar to boil 10 c.c. of the standard solution with 40 c.c. of distilled water just for a few minutes, in order to make sure that such treatment causes no turbidity or distinct precipitation.

**The Solution of Sugar.**—It is important that the liquid should not be dark in colour, because the pale blue tint of an excess of copper solution would not be visible in a yellow or brown mixture.

Solutions may frequently be decolourised by heating a measured volume to boiling, adding a few drops of milk of lime, allowing the precipitate to settle, filtering through animal charcoal, and diluting the washings to a definite volume. The animal charcoal may be of the granulated kind used by sugar refiners, and is conveniently used by half-filling a tube 18 inches in length, which is drawn out at the lower end to a point with a narrow opening. When the tube is fixed upright in a stand the liquid is poured in, and there being a column of considerable length its passage through the filter is rapid.

**The Method of Analysis.**—10 c.c. of the solution are accurately measured with a pipette, and transferred to a white porcelain dish about 5 inches in diameter, or a flask of convenient size; 40 c.c. of distilled water are added, and if necessary a like volume of caustic soda solution. The liquid is boiled. The suitably diluted sugar solution is delivered from a burette at first in portions of 1 c.c., boiling the liquid after each addition. When the precipitate which forms is seen to be of a bright red colour, the lamp should be removed in order that the precipitate may settle. It is necessary now to observe the depth of blueness in the liquid, which is done by tilting the white basin and looking at the edge of the solution. If a flask is used it should be held up to the light before a window. As long as any blue tint remains, more sugar solution must be added and the

liquid boiled again. When in doubt a small quantity of the *hot* solution may be filtered, acidified with acetic acid, and tested for copper with a drop of potassium ferrocyanide, which will give either a brown coloration or a precipitate, according as a small or large excess of copper solution is present.

It must not be expected that the exact point when the reaction terminates can be ascertained on the first occasion. The operation should be repeated; nearly the whole of the necessary volume of the sugar solution being measured into a beaker, boiled, and in a gently continuous stream added at once; the beaker is rinsed with boiling water, and the rinsings added to the copper solution, then the finishing of the process is carried out as quickly as is consistent with accuracy to prevent the hot solution being exposed to the atmosphere for a period longer than necessary. The boiling should not be prolonged beyond twelve or fourteen minutes if the solution is likely to contain any dextrine. To discharge the colour from 10 c.c. of copper solution 0.05 gram of glucose is necessary; hence the volume of solution used contained this quantity.

*Example.* — A specimen of urine was examined; 35 c.c. were required to decolourise 10 c.c. of copper solution;

hence 
$$\frac{0.05 \times 100}{35} = 0.14 \text{ gram.}$$

The liquid contained 0.14 gram of glucose in 100 c.c., or 1.4 gram per litre.

If the urine is too strong in sugar, as is frequently the case, 10 c.c. may be diluted to 200 c.c., and the quantity of sugar found as above multiplied by 20.

The sugars which directly reduce Fehling's solution are maltose, milk sugar, dextrose, lævulose, and sugar in the urine of patients suffering from *diabetes mellitus*.

The first two of these sugars differ from the others in belonging to the saccharose group. Maltose occurs in beer wort and distillers' mash. Its reducing power is only two-thirds that of glucose, so that 10 c.c. of copper solution represent 0.0757 gram of maltose.

Cane, maple, and beet sugar do not act upon Fehling's solution directly, but they may be converted into glucose by heating 30 c.c. or 40 c.c. of the clarified solution with thirty or forty drops of dilute sulphuric acid (1 to 5) for twenty minutes. The liquid must be maintained at a constant volume by the addition of as much water as may be necessary, otherwise the sugar will become brown. The acid is neutralised with sodium carbonate, and diluted to twenty times its volume before titration. The effect of the acid is hydration or hydrolysis of the saccharose, and the production therefrom of dextrose and lævulose. The precise reason for this effect of the acid is not known. 100 parts of glucose represent 95 parts of saccharose, or 10 c.c. of copper solution are

reduced by 0.0475 gram of saccharose from the cane or beet.

Milk sugar may also be converted into glucose by boiling with dilute sulphuric acid.

### 33. THE ANALYSIS OF URINE.

#### **Estimation of Chlorides, Phosphoric Acid, Sugar, Free Acid, and Ammonia.**

**Chlorides.**—10 c.c. of urine are mixed with about 5 c.c. of deci-normal permanganate solution and 40 c.c. of water. The mixture is boiled, whereby the organic matter present is decomposed and a brown flocculent precipitate results. Filter, and, if the liquid is colourless, add one drop of the permanganate solution, so as to communicate a rose colour to the solution. Remove the excess of permanganate by adding a few drops of a solution of oxalic acid, carefully avoiding an excess. Two drops of a solution of neutral potassium chromate are added, and the mixture is titrated according to the method described on p. 115. If the urine is pale in colour the chromate may be added and the titration proceeded with at once; but as the organic matter carries down a little silver, the resulting figures are not so accurate.

**Phosphoric Acid.**—This is determined by means of a standard solution of uranyl acetate (see 31, p. 132) which

has been titrated and its strength determined by means of a standard solution of sodium phosphate, which, however, need not be converted into calcium phosphate. 50 c.c. of the clear urine are measured into a small beaker, together with 5 c.c. of the solution of sodium acetate. The solution is warmed on the water-bath. Should too much uranium solution be accidentally added, an additional 10 or 20 c.c. of the same urine may be placed in the beaker and the titration again proceeded with more cautiously.

**Sugar.**—This is estimated with Fehling's solution (see 32); 10 c.c. of the urine are made up to 200 c.c. in a measuring flask and titrated against 10 c.c. of copper solution. In calculating the amount of sugar make allowance for the liquid being diluted twenty times.

**Free Acid.**—100 c.c. of the urine are measured into a beaker and cautiously titrated with a deci-normal solution of sodium hydrate prepared from the metal. The point of neutrality is tested by a drop of the liquid taken upon the point of a glass rod and applied to some sensitive violet litmus-paper. It should cause no change in its colour. As the acidity cannot be attributed to any one acid in particular, but is generally largely due to uric acid, it is usual to describe it as being equivalent to the quantity of caustic soda contained in the volume of the normal solution used.

**Ammonia,**—The 100 c.c. of the urine which have

been neutralised with soda are put into a flask holding about half a litre ; 10 c.c. of a solution of normal soda measured in a pipette are added, and the liquid is boiled cautiously in order that the frothing be not so great as to cause bubbles to pass out of the neck of the flask. When no more froth is formed, boiling is allowed to continue quietly until all traces of ammonia have ceased to come off with the steam. The flask is allowed to cool down to a convenient temperature, the contents are transferred to a beaker, and normal nitric acid is added while the mixture is constantly stirred. The point of neutrality is tested as in the case of the determination of free acid. The volume of normal acid used is deducted from the 10 c.c. of alkali, and each c.c. of the remainder = 0.017 gram of ammonia. This process is not applicable to stale urine, as it contains ammonium carbonate resulting from the decomposition of urea.



## TECHNICAL ANALYSIS.

### 34. COAL.

**Estimation of Moisture.**—About 2 grams of the coal are quickly powdered and placed without loss of time between watch-glasses previously weighed. Thus the initial weight of the coal is taken. It is dried at a temperature ranging from  $105^{\circ}$  to  $110^{\circ}$  C., but not higher, otherwise it might part with other volatile matter than water, and at elevated temperatures it is apt to gain in weight.

**Ash.**—About 1 gram of the coal is very finely powdered and ignited in a platinum crucible, heat being applied very gently at first, so as to drive off volatile matter without causing the coal to cake more than is unavoidable. The crucible should be fitted into a hole made in a piece of asbestos cardboard. The crucible or the cardboard itself may be placed at an angle of  $30^{\circ}$  to the vertical position. In this way the gases from the burner are separated from the heated air, which finds its way into the crucible. In order to calcine the ash completely, it may be moistened with alcohol after incineration and ignition continued. In this way combustion may be greatly accelerated.

Another good method of burning off the carbon is to place the crucible in a very hot muffle furnace. If necessary, the combustion may be completed in a stream

of oxygen freed from chlorine by passing it through caustic potash-solution. Proceeding in this way with asbestos cardboard, the carbon should be entirely consumed in two hours; otherwise, without the aid of a muffle or a stream of oxygen, it is difficult to obtain a pure ash even after heating for eight or ten hours. The use of a blow-pipe or blast-lamp is not to be recommended, as alkalies may be volatilised, and there is a risk of loss through mechanical causes. With coke and anthracite the material may be coarsely powdered and heated in a platinum boat previously weighed, and weighed with the substance in it, the heating to be conducted in a combustion furnace in a stream of oxygen, the boat being enclosed in a hard glass combustion tube or in a tube of porcelain.

**Volatile Matter and Coke.**—A sample of the coal amounting to 20 or 30 grams is weighed in a previously weighed porcelain crucible with a lid. There should be ample room in the crucible; it should in fact be not more than one-third filled. The porcelain crucible should be placed in a roomy fire-clay crucible and entirely surrounded and covered over above the lid with pieces of charcoal; a lid is placed on the clay crucible, and the whole is strongly heated in a furnace for an hour. The porcelain crucible is removed, dusted, and weighed. The loss is moisture, volatile matter, and sulphur. The residue is coke and ash.

**Another Method.**—1 gram of finely powdered coal is placed in a platinum crucible at least  $1\frac{1}{4}$  inch deep, provided with a closely fitting lid. The crucible must then be heated by means of a Bunsen burner, the flame of which should not be less than 7 inches high. The crucible should be supported on a triangle of thin platinum wire, and it should be so placed that the space between the bottom of the crucible and the top of the tube of the burner is not more than  $1\frac{1}{4}$  inch. The flame should not be disturbed by draughts. In this way it entirely surrounds the crucible and prevents the access of air to the contents. The heating ought not to last longer than a few minutes, but must be continued as long as any appreciable quantity of inflammable matter escapes. If the flame be of smaller dimensions or the crucible supported by a stout triangle, the yield of coke will be too high. The results should be always calculated upon coal or coke free from ash, if it is desired to make comparisons between a number of different samples. For use in reverberatory furnaces good coal should yield from 60 to 70 per cent of coke.

**Sulphur.**—A sample of the coal weighing about 1 gram is very finely powdered and intimately mixed with four times its weight of anhydrous sodium carbonate, perfectly free from sulphate, in a large platinum basin or crucible. The mixture is made by stirring with a dry

glass-rod; the powder should not be pressed or shaken down. The platinum vessel is loosely covered, if a basin, with a piece of platinum foil or asbestos card-board. Heat is applied at first so gently as not to volatilise hydrocarbons; in other words, there should be no smell perceptible, or only a faint aromatic odour. If the coal-gas is well purified, a Bunsen burner may be employed, the form known as an Argand-Bunsen answering the purpose well. Otherwise an Argand spirit-lamp should be used to avoid the possibility of sulphur dioxide or sulphuric acid, resulting from the combustion of the gas being absorbed by the alkali. The temperature should be maintained below a red-heat for some time, but it should be increased very gradually without attaining visible redness, until the dark grey colour of the surface of the mixture becomes a very light grey. The temperature is then raised to a feeble red-heat and maintained for forty to sixty minutes. The mixture will become quite white or reddish if iron be present, showing that the coal has been completely decomposed. The mass is next treated with water, boiled, filtered, cautiously acidified with hydrochloric acid, and the sulphur which has been converted into sulphate precipitated by barium chloride. The barium sulphate is treated in precisely the same way as for the estimation of sulphuric acid in other substances. The operation is finished in an hour and a half.

*Notes.*—(1.) It is important to bear in mind that for the estimation of sulphur minute pulverisation is essential. It is safest to sift the powdered coal through calico or fine muslin.

(2.) Should particles of coal remain unoxidised, the mass may be fused and a very little nitre added.

(3.) The sulphur in coke may be estimated in the same way.

(4.) The combustion of the coal travels from the surface downwards, and the spaces between the particles of alkali seem to act as chimneys. Hence stirring the mixture during the oxidation retards the process instead of hastening it.

*Example.*—A sample of caking coal. The analysis was made in duplicate.

### Estimation of Moisture—

	I.	II.
Weight of coal + crucible .	= 22·3727	23·0108
Weight of crucible .	= 21·6322	21·6310
Coal taken	= <u>0·7405</u>	<u>1·3798</u>

I. Dried at 100° C., 1st weighing = 22·3352

„ „ 2d „ = 22·3335

„ „ 3d „ = 22·3370

II. Dried at 100° C., 1st weighing = 22·9424

„ „ 2d „ = 22·940

„ „ 3d „ = 22·9392

The 3d weighing of Sample I. shows a slight increase, probably due to absorption of oxygen as already mentioned; the 2d weighing was therefore regarded as the more correct for the dry coal.

Weight of crucible and coal before heating . . . .	I.	II.
	= 22.3727	23.0108
Weight of crucible and coal after heating . . . .		
	= 22.3335	22.9392
Loss = water	= 0.0392	0.0716

I.	II.
Per cent.	Per cent.
$\frac{0.0392 \times 100}{0.7405} = 5.29$	$\frac{0.0716 \times 100}{0.7405} = 9.66$
moisture	

### Ash—

Weight of coal + crucible . . . .	I.
	= 14.0625
Weight of crucible . . . .	
	= 12.9675
Coal taken	= 1.095
After ignition—	
Weight of crucible + ash . . . .	I.
	= 12.9960
Weight of crucible . . . .	
	= 12.9675
Weight of ash	= 0.0285
I.	II.
Per cent.	Per cent.
$\frac{0.0285 \times 100}{1.095} = 2.60$	$\frac{0.0285 \times 100}{1.095} = 2.94$
ash.	ash.

**Volatile Matter and Coke—**

I.

$$\text{Weight of coal taken} \quad . \quad . \quad = \underline{\underline{30.8575}}$$

After heating—

I.

$$\text{Weight of crucible and contents} \quad . \quad = 47.8455$$

$$\text{Weight of crucible} \quad . \quad . \quad = \underline{29.9150}$$

$$\text{Weight of coke and ash} \quad = \underline{\underline{17.9305}}$$

I.

$$\frac{17.9305 \times 100}{30.8575} \text{ Per cent.} = \underline{\underline{58.10 \text{ coke and ash.}}}$$

Coke and Ash.      Ash.      Per cent.

$$58.10 - 2.60 = \underline{\underline{55.50 \text{ coke.}}}$$

Weight of Coal.      Coke and Ash.      Volatile Matter and Moisture.

$$30.8575 - 17.9305 = 12.927.$$

I.

$$\frac{12.927 \times 100}{30.8575} \text{ Per cent.} = \underline{\underline{41.89 \text{ volatile matter and moisture.}}}$$

I.

Per cent.

$$\text{Volatile matter and moisture} \quad . \quad . \quad = 41.89$$

$$\text{Moisture} \quad = \underline{5.29}$$

$$\text{Volatile matter} \quad = \underline{\underline{36.60}}$$

**Sulphur—**

	I.	II.
Quantities of coal taken .	= 0.5874	0.6195
BaSO <sub>4</sub> obtained . . .	= 0.1606	0.1682
Sulphur per cent	= 3.75	3.72

**Composition of the Coal—**

	I.	II.
	Per cent.	
Coke . . .	55.50	...
Volatile matter .	36.60	...
Ash . . .	2.60	2.94
Moisture . . .	5.29	5.189
	99.99	

	I.	II.
	Per cent.	
Sulphur . . .	3.75	3.72

**35. PYRITES.**

**Moisture.**—The ground pyrites is dried at 105° C. till the weight remains constant.

**Sulphur.**—About 0.5 gram of pyrites, without previously drying, is treated with about 10 c.c. of a mixture of three volumes nitric acid (sp. gr. 1.4) and one



volume strong hydrochloric acid, both ascertained to be absolutely free from sulphuric acid. The reaction should be made in a porcelain basin capable of holding at least 150 c.c., the liquid being covered with an inverted funnel about 4 inches in diameter. In this way fumes escape and spiriting is prevented. Heat up the mixture now and then, evaporate to dryness in a water-bath, add 5 c.c. hydrochloric acid, evaporate once more. Add 1 c.c. concentrated hydrochloric acid and 100 c.c. hot water, filter through a small filter, and wash with hot water. The insoluble residue may be dried, ignited, and weighed. It may contain silicic acid and silicates, the sulphates of barium, lead, and even calcium; the sulphur of sulphates, being useless for the purpose of sulphuric acid-making, is not estimated. The filtrate and washings are made alkaline with ammonia, excess being avoided. The precipitated ferric hydrate is filtered and washed. This can be done within an hour's time by employing the following precautions: (1) Filter hot, and wash on the filter with hot water, avoiding channels in the mass of precipitate, but so that the whole precipitate is thoroughly churned up with the water each time (washing by decantation would produce too great a bulk of liquid); (2) Employ a sufficiently dense paper capable of filtering rapidly, such as No. 595, mentioned on p. 11; (3) Use funnels, made at an angle of exactly  $60^\circ$ , the tube being not too wide, and *com-*

*pletely filled* by the liquid running through. A filter-pump may also be employed with the usual precautions. Wash till about 1 c.c. of the washings, on adding barium chloride, shows no opalescence even after a few minutes. The filtrate and washings should not exceed 200 c.c., otherwise they should be concentrated by evaporation. Acidulate with pure hydrochloric acid in *very slight excess*, boil, remove the burner, and add a solution of barium chloride just previously boiled. For 0.5 gram pyrites 20 c.c. of a 10 per cent solution of barium chloride is always more than sufficient. This may be roughly measured in a test-tube provided with a mark, and it may be heated in the same tube. After precipitation the liquid is left to stand for half an hour, by which time the precipitate should have completely settled. Decant the clear portion through a filter, pour 100 c.c. boiling water on to the precipitate, and stir up. Wait two or three minutes for the precipitate to settle completely, and decant again. Repeat the washing with boiling water, and the decantation three or four times, till the liquid has lost its acid reaction. Wash the precipitate on to the filter, dry, and ignite. It should be a perfectly white and loose powder. One part of it is equal to  $\frac{32 \times 1}{233} = 0.1373$ , where sulphur Ba = 137, S = 32, O = 16, and BaSO<sub>4</sub> = 233.

**Copper.**—1 gram of pyrites, finely powdered and

dried as before, is treated with concentrated nitric acid, and then evaporated to dryness. Pour concentrated sulphuric acid over the residue, and heat on a sand-bath till the free acid is expelled. Let it cool down, boil up the mass with water, allow it to cool, add a quarter of its volume of spirit of wine, let it stand for twelve hours, and filter. The residue on the filter is washed with a mixture of 1 part alcohol and 2 parts water till the filtrate is free from copper. The dilute filtrate is saturated with sulphuretted hydrogen, and allowed to stand for some hours. The precipitate (containing the sulphides of copper, arsenic, antimony, and bismuth) is washed with a solution of sulphuretted hydrogen containing a little sulphuric acid, dried, mixed with the ashes of the filter, which has been previously burnt, and with pure sulphur (recrystallised from carbon disulphide) ignited in a Rose's crucible in a current of hydrogen or coal-gas, and weighed. In this operation arsenic is completely volatilised; antimony and bismuth remain along with the copper. Spanish pyrites contains an almost constant quantity of 0.05 per cent of antimony and bismuth, of which 0.0005 gram, together with the weight of the filter-ash, is deducted from the cuprous sulphide. Where  $\text{Cu} = 63.33$  and  $\text{S} = 32$ , then

$$1 \text{ part of } \text{Cu}_2\text{S} = \frac{126.66 \times 1}{158.66} = 0.7983 \text{ Cu.}$$

### 36. PYRITES CINDER.

Sulphur is estimated by dissolving the substance in aqua regia, evaporating with hydrochloric acid, dissolving in a very little hydrochloric acid and hot water, and precipitating with barium chloride while the solution is boiling, as described in 35.

Copper is estimated as already described in 35, but the solution of the sample (1 gram) is made by means of hydrochloric acid, with a few drops of nitric acid. A deduction of 0.07 per cent for bismuth and antimony is made from the percentage of copper found.

*Note.*—The iron is previously precipitated in 35 in order that the barium sulphate may not carry down any basic ferric salt on the addition of barium chloride. It is not necessary to estimate the sulphur with such great accuracy in pyrites cinder as in unburnt pyrites; the treatment with ammonia is therefore here omitted.

### 37. COMPLETE ANALYSIS OF CALCIUM SUPERPHOSPHATE.

**Moisture.**—Weigh about 2 grams of the superphosphate between a pair of weighed watch-glasses, and dry in a water-oven at  $100^{\circ}\text{C}$ . until the weight is constant. The loss represents moisture.

**Combined Water.**—The substance dried at  $100^{\circ}$  is further heated in an air-bath to  $150^{\circ}$ , cooled in a desiccator, weighed, and the heating repeated until it ceases to lose weight. This second loss represents chemically combined water.

**Insoluble Mineral Matter.**—The dried substance is transferred to an evaporating basin, every particle being brushed off the watch-glass with a camel's-hair brush. Strong hydrochloric acid is poured on to the substance, and some water is added. Heat is applied until the action of the acid has ceased. The solution is then filtered, and the insoluble residue well washed with hot water, dried, ignited, the filter-paper burnt, and the crucible with contents weighed.

**Soluble Phosphoric Acid.**—Weigh out exactly 20 grams of the original substance, and triturate with cold water, in a mortar, the small lumps being broken up. It is best to add only sufficient water at first to make the phosphate into a paste, and afterwards to add the water

little by little, continuing to triturate. The bulk of the liquid is poured on to a filter in a litre flask, more water is added, and trituration is continued, the liquid being filtered a second time. The operation is repeated a third and a fourth time. The residue is then washed into the litre flask, and the flask is filled to three-fourths of its capacity. Allow it to stand for three hours, occasionally shaking to agitate the liquid and residue at intervals. The liquid is filtered into a litre flask, the residue being washed with water sufficient to fill the second flask up to the mark. The liquid must now be thoroughly mixed, which may be done by transferring it to a dry quart jug and stirring with a strip of glass.

Of this solution 50 c.c. are transferred to a beaker, and dilute caustic soda is added until the reaction is just alkaline; a white flocculent precipitate then forms. Acetic acid is added until the reaction is strongly acid. That is to say, not only must the originally acid reaction be restored, but a few more drops of acetic acid must be added. If a slight, white flocculent precipitate of ferric phosphate still remains undissolved, it may be collected on a filter, washed well, dried, ignited, and weighed. From its weight the ferric oxide and phosphoric anhydride are calculated.

As, however, more or less lime is carried down with the alumina and ferric phosphate, this should, when possible, be separated. Dissolve the precipitate in

strong hydrochloric acid, add a little citric acid to retain ferric oxide and alumina in solution, neutralise the solution with ammonia, add a slight excess of acetic acid, and precipitate any lime which may be present by adding ammonium oxalate. Filter, wash, ignite intensely, and weigh as caustic lime,  $\text{CaO}$ .

The filtrate from the iron and alumina may be concentrated and afterwards filled up to 50 c.c. To this liquid 5 c.c. of a solution of sodium acetate are added, and the phosphoric acid is determined with a standard solution of uranyl acetate which has previously been standardised with a solution of tricalcic phosphate. Nearly the full amount of uranium solution should be added before heat is applied to the liquid, in order to prevent any precipitation of calcium phosphate (see p. 134).

**Insoluble Phosphoric Acid.**—About 2 grams of the finely powdered substance are heated on the water-bath, with 50 c.c. of water and 10 c.c. of nitric acid in a 250 c.c. flask until dissolved. A small quantity of matter remains undissolved. The liquid is allowed to cool, and the flask is filled up to the 250 c.c. mark. Shake well and filter. Of this solution 50 c.c. are measured off and titrated as before with uranic acetate. On deducting the amount of soluble phosphate, already ascertained, from the total phosphoric acid, the difference gives the phosphoric acid in the insoluble phosphate.

**Sulphuric Acid.**—Of the acid solution 50 c.c. are measured off and precipitated by barium chloride in the usual manner (see 9, p. 51).

**Lime.**—50 c.c. of the acid solution are mixed with caustic soda until the reaction of the liquid is alkaline, then acetic acid is added until the precipitated lime and magnesia phosphate are redissolved. The ferric phosphate is filtered off and well washed. The filtrate is heated, and ammonium chloride, ammonia, and ammonium oxalate are added, and the liquid with the precipitate is allowed to stand over-night, the clear supernatant liquid is syphoned off and filtered if necessary, and the precipitate is washed well with hot water, the wash water is filtered, the precipitate is washed on to the filter and again washed with hot water, dried, ignited, the paper burnt, and the whole weighed as carbonate, the instructions on p. 78 being observed.

**Magnesia.**—The filtrate from the calcium oxalate is next made strongly alkaline with ammonia. The precipitate and liquid are allowed to stand over-night, filtered, and the precipitate is treated in the usual manner (see 15, p. 71).



## ANALYSIS OF SUPERPHOSPHATE OF LIME.

	I.	II.
	Per cent.	Per cent.
Magnesia . . . .	0·51	0·43
Lime . . . .	24·68	24·69
Sulphuric acid . . .	32·09	31·84
Moisture expelled at 100° C. .	14·32	13·83
Combined water . . .	3·88	4·62
Insoluble matter . . .	4·29	4·29
Ferric oxide . . . .	0·61	0·61
Soluble phosphoric acid .	18·13	18·22
Insoluble phosphoric acid .	0·62	0·59
Organic matter (not estimated)	...	...
	<u>99·13</u>	<u>99·12</u>



METHODS OF ANALYSING ALLOYS  
AND COMPLEX MINERALS



## REMARKS ON THE PRECIPITATION OF ZINC.

Many alloys contain zinc in large or small proportion. In the analysis of such the separation of this metal has generally proved troublesome, and to obviate any difficulty a volumetric method of estimating the zinc has been much used. The use of a method of separation and weighing of a definite zinc compound, when only two or three analyses have to be made, is much to be preferred. On examining the processes for the precipitation of zinc sulphide, in **Examples 38, 40 (c)**, p. 185, **40 (e)**, p. 187, and **41**, p. 191, it may be remarked that the one described in **40 (e)** and **41** is most to be recommended for convenience, though all have given good results, as the figures indicate.

### 38. BRASS.

#### **Estimation of Copper and Zinc, with Small Quantities of Lead and Iron.**

Accurately weigh out about 5 grams of the alloy in the form of wire, turnings, filings, or clippings, and dissolve it in nitric acid, evaporate to dryness, add some strong hydrochloric acid, evaporate again, and dissolve up with dilute hydrochloric acid and a little water so as

to form an acidulated aqueous solution. Boil and pass sulphuretted hydrogen through the liquid for some time, allow the precipitate to subside, decant the solution on to a large filter. Dilute the filtrate with an equal volume of water, boil, and again pass the gas, treating the precipitate, if any, as before. Wash the mixed precipitates with hydrochloric acid of specific gravity 1.05 saturated with sulphuretted hydrogen. Then wash several times with sulphuretted hydrogen water, finally pour the precipitate on to the filter and allow it to drain. The precipitate contains copper, lead, and a trace of arsenic ; the filtrate, zinc and iron.

This precipitate must not be kept or exposed to the air for any length of time, because copper sulphide is easily oxidisable and converted into sulphate.

Remove the precipitate from the filter as completely as possible by means of a glass rod into a porcelain basin, wash in the remainder, and evaporate on a water-bath. Treat the filter in a separate dish with nitric acid diluted with an equal volume of water, pour this solution on a small filter, and wash the original filter, which may afterwards be thrown away. The acid is then introduced into the porcelain basin containing the sulphides ; invert a funnel over the basin to prevent loss by spirting, and digest on a water-bath till the separated sulphur is of a light yellow colour. This solution of the sulphide is then poured on to a small filter as before, and

the filtrate is received in a porcelain dish. The filter, with the sulphur, is then dried and ignited, the residue is treated with strong nitric acid and filtered into the remaining solution.

**Separation of the Lead.**—Dilute sulphuric acid is added in slight excess to the liquid, and evaporation is carried on till sulphuric acid begins to volatilise. The residue is then dissolved with water containing a little sulphuric acid, heated and poured on to a weighed filter (p. 19), if the amount be very small, the filtrate being received in a litre flask.

The residue, consisting of lead sulphate, is washed free from copper with water acidulated with sulphuric acid, and finally with strong alcohol, such as redistilled methylated spirit. The alcoholic washings must be kept separate, but that portion of the liquid containing copper is added to the litre flask. The filtrate and aqueous washings are then made up to 1 litre. This solution contains all the copper, and the amount must be determined subsequently.

**Separation of Zinc and Iron in the Filtrate.**—The filtrate from the precipitate caused by sulphuretted hydrogen is evaporated to expel the greater part of the acid, boiled with a few drops of nitric acid and filtered into a flask; then barium carbonate is added and the flask is corked. After standing for some hours the precipitate is filtered off.

- (a) The precipitate contains  $\text{Fe}_2\text{O}_3$  and  $\text{BaCO}_3$ .
- (b) The filtrate contains  $\text{ZnCl}_2$  and  $\text{BaCl}_2$ .
- (a) The precipitate is dissolved in hydrochloric acid, and the iron is precipitated by addition of ammonia. The liquid is heated and filtered, and the precipitate ignited and weighed as  $\text{Fe}_2\text{O}_3$ .

To completely precipitate the zinc the following operations are necessary :—

- (b) The filtrate is introduced into a flask of about half a litre capacity and fairly diluted with water, add some ammonium chloride, nearly neutralise the liquid with sodium carbonate, boil for a short time, and to the hot solution add just a sufficiency of freshly prepared and colourless ammonium sulphide, containing an excess of ammonia until the liquid is alkaline. There must be no great excess of the sulphide present. Fill the flask up with water, cork, and allow it to stand for twelve hours in a warm place. Filter the liquid while hot, cover the funnel with a glass plate, and wash the precipitate with water containing ammonium sulphide and a gradually decreasing quantity of ammonium chloride until there is none. Dissolve the precipitate in hydrochloric acid, precipitate with sodium carbonate, filter, ignite, and weigh as  $\text{ZnO}$ .



**Estimation of the Copper.**—Take 100 c.c. of the solution in the litre flask, evaporate to expel nitric acid, a little strong hydrochloric acid being added to convert the salt into chloride, dilute with water to the original volume, pass sulphuretted hydrogen through the liquid, warm, again pass the gas and filter. Wash the precipitate with water containing sulphuretted hydrogen and dry. The dried precipitate is then transferred to a porcelain crucible, the filter is burnt and added, and some pure sulphur is mixed therewith. A cover with a hole in the centre is provided for the crucible, and through this a porcelain tube delivers a stream of hydrogen into the crucible. The crucible is ignited, cooled, and weighed. The ignition is repeated, a further small addition of sulphur being made until the weight is constant.

The contents of the crucible are weighed as  $\text{Cu}_2\text{S}$  and multiplied by 10 as representing only  $\frac{1}{10}$  of the copper in the alloy.

*Example—*

Weight of brass taken . . . = 6.136 grams.

**Lead—**

	Grams.
Weight of $\text{PbSO}_4$ , filter, and weighing-tube	= 16.9600
Weight of filter and weighing-tube . . .	= 16.9235
	<hr/>
Weight of $\text{PbSO}_4$	= 0.0365
	<hr/>

To find the percentage of lead—

$$\text{Pb} = 207$$

$$\text{S} = 32$$

$$\text{O}_4 = 64$$

$$\hline$$

$$303$$

$$\hline$$

$$\frac{0.0365 \times 207}{303} = 0.0249 \text{ gram.}$$

$$\frac{0.0249 \times 100}{6.136} \text{ Per cent.} = 0.405 \text{ lead.}$$

**Iron—**

	Grams.
Weight of $\text{Fe}_2\text{O}_3$ crucible, lid, and filter-ash	= 40.6177
Weight of crucible, lid, and filter-ash	= 40.5485
Weight of filter-ash	= 0.0060

$$\hline \text{Weight of } \text{Fe}_2\text{O}_3 = 0.0632 \hline$$

To find the percentage of iron—

$$\text{Fe}_2 = 112$$

$$\text{O}_3 = 48$$

$$\hline$$

$$160$$

$$\hline$$

$$\frac{0.0832 \times 112}{160} = 0.0442 \text{ gram.}$$

$$\frac{0.0442 \times 100}{6.136} \text{ Per cent.} = 0.72 \text{ iron.}$$

**Zinc—**

	Grams.
Weight of $\text{ZnO}$ + crucible, lid, and filter-ash	= 25.547
Weight of crucible + lid	= 23.236
Weight of filter-ash	= 0.006

$$\hline \text{Weight of } \text{ZnO} = 2.305 \hline$$

To find the percentage of zinc—

$$\begin{array}{rcl}
 \text{Zn} = 65.5 & & 2.305 \times 65.5 \\
 \text{O} = 16 & & \underline{\quad\quad\quad} \\
 & & 81.5 \\
 & & \underline{\underline{\quad\quad\quad}} \\
 & & 81.5
 \end{array}
 \qquad
 \frac{1.852 \times 100}{6.136} \text{ Per cent.} = 30.18 \text{ zinc.}$$

**Copper.**—Only  $\frac{1}{10}$  of the solution of the substance was used for the estimation of copper.

Weight of $\text{Cu}_2\text{S}$ + crucible and filter-ash	.	.	.	.	= 10.881
After reheating (1)	.	.	.	.	= 10.872
„ „ (2)	.	.	.	.	= 10.8625
„ „ (3)	.	.	.	.	= 10.862
Weight of $\text{Cu}_2\text{S}$ , crucible, and filter-ash	.	.	.	.	= 10.862
Weight of crucible + filter-ash	.	.	.	.	= 10.329
<hr/>					
Weight of $\text{Cu}_2\text{S}$ + filter-ash	.	.	.	.	= 0.533
Weight of filter-ash	.	.	.	.	= 0.006
<hr/>					
Weight of $\text{Cu}_2\text{S}$					= 0.527
<hr/>					

To find the percentage of copper—

$$\begin{array}{rcl}
 \text{Cu}_2 = 127 & & \\
 \text{S} = 32 & & 0.527 \times 127 \text{ Gram.} \\
 & & \underline{\quad\quad\quad} \\
 & & 159 \\
 & & \underline{\underline{\quad\quad\quad}} \\
 & & 159
 \end{array}
 \qquad
 \frac{\quad\quad\quad}{159} = 0.4209 \text{ copper.}$$

But 0.4209 gram of copper is only  $\frac{1}{10}$ , therefore the actual amount present in the quantity of alloy taken for analysis = 4.209 grams.

$$\frac{4.209 \times 100}{6.136} \overset{\text{Per cent.}}{=} 68.59 \text{ copper.}$$

	Per cent.
Lead .	0.40
Iron .	0.72
Zinc .	30.18
Copper	68.59
	<hr/>
	99.89
	<hr/>

*Notes.*—(1.) Copper sulphide is easily dissolved by nitric acid, and some sulphur generally separates, which entangles a little of the copper sulphide, thus preventing it entering into solution.

(2.) There should not be too large a proportion of hydrochloric acid, lest some of the lead be retained in solution when submitted to the action of sulphuretted hydrogen. To guard against this, dilution and a second treatment with sulphuretted hydrogen are advisable.

(3.) Small quantities of zinc sulphide are precipitated along with arsenic sulphide; but as zinc sulphide is easily soluble in hydrochloric acid, it may be removed by washing the precipitate

with this acid, mixed with a solution of sulphuretted hydrogen.

- (4.) To completely precipitate copper from a strong solution sometimes half an hour is not too long for the gas to be passed through the liquid.
- (5.) The foregoing description states that hydrogen is passed into the crucible when the copper sulphide is heated, and, in the analysis quoted, hydrogen was actually employed; but it is worth recording that coal-gas may conveniently be used instead.
- (6.) The precipitate of zinc sulphide obtained in the manner here described cannot be properly washed unless *ammonium chloride* be added to the water. Without such addition the filtrate is always turbid, even though ammonium sulphide be used.
- (7.) If tin be present, dissolve 2 grams in nitric acid, *evaporate to dryness* on the water-bath, moisten with nitric acid, add water and warm, dilute still further, and filter off any stannic oxide, as in 39. The filter is acidified with 20 c.c. of dilute sulphuric acid; evaporated on the water-bath and diluted with 50 c.c. of water; warm and filter off any lead sulphate. This must be treated as already described. The filtrate may be treated for the separation

of copper from zinc and iron. Dilute conveniently and boil, then add a strong solution of sodium thiosulphate as long as a black precipitate forms. As soon as this has subsided, leaving only sulphur in suspension, the precipitation of copper is complete. For the treatment of the precipitate (see 39, p. 175).

### 39. BRONZE COINAGE, GUN METAL, BELL METAL.

#### Estimation of Lead, Tin, Zinc, and Copper.

A halfpenny is fixed in a hand or table vice, and with a clean file a quantity of the metal is finely divided, the filings falling on to a sheet of glazed writing-paper. Transfer 5 grams of the filings accurately weighed from a tube into a flask capable of holding from half a litre to a litre. A small funnel is placed in the neck of the flask, through which some moderately strong nitric acid of 1.3 sp. gr. is gradually poured on to the filings. When the first tumultuous evolution of gas has moderated, the flask is gently warmed until the stannic oxide formed appears of a white colour, and no further action of the acid appears to take place. The contents of the flask are then transferred to a porcelain basin and evaporated *to complete dryness*, in order to

secure the insolubility of the stannic oxide. Water is then added, the precipitate is filtered off and washed until the washings scarcely redden litmus-paper. The precipitate is then dried, transferred to a weighed porcelain crucible, the precipitate is ignited, the filter burnt and added to the crucible, the whole once more ignited over a blast-lamp or blow-pipe, cooled, and then weighed as  $\text{SnO}_2$ . A strong ignition is necessary, since a simple red-heat is not sufficient to completely dihydrate the stannic oxide. The filtrate contains the other metals as nitrates.

**The Estimation of Lead.**—Add some sulphuric acid to the filtrate in fair excess, transfer the mixture of lead sulphate and solution of salts to an evaporating basin, evaporate till fumes of sulphuric acid are freely evolved, allow the liquid to cool, and add water. Filter immediately from the undissolved lead sulphate, wash with water containing sulphuric acid, remove the beaker containing the filtrate, and replace it by another vessel. The sulphuric acid in the filter-paper must now be displaced by washing with alcohol, the filter and precipitate are dried, the precipitate, if sufficiently large, is transferred to a crucible, the paper burnt and added thereto, and the whole ignited. Weigh as  $\text{PbSO}_4$  and calculate as Pb.

**The Estimation of Copper.**—The filtrate from the lead sulphate containing copper and zinc sulphates is nearly neutralised with sodium carbonate, diluted to about

700 c.c., boiled, and mixed with a strong solution of sodium thiosulphate as long as a black precipitate falls. The precipitate, which is cuprous sulphide, is allowed to subside, a little sulphur remains in suspension in the liquid, the precipitate is filtered off and washed. As it is not readily oxidised, it is unnecessary to use the precautions employed when washing the cupric sulphide. The precipitate is washed out of the filter as far as possible into an evaporating basin of 4 or 5 inches diameter, with a stream of hot water from a washing bottle, and then digested with nitric acid. The filter is separately treated in a beaker or evaporating basin with nitric acid, and filtered free from the paper fibres and transferred to the cupric nitrate; a sufficiency of sulphuric acid is then added and the liquid evaporated until fumes of sulphuric acid are evolved. The liquid is cooled and diluted with water, transferred to a litre flask, and the basin repeatedly rinsed until no more copper is removed by the rinsings; it is then made up to 1 litre. An accurately graduated pipette, capable of delivering 100 c.c., is then filled with the solution after it has been completely mixed, and three separate quantities of the solution are removed. The copper is precipitated by sodium thiosulphate, washed, ignited with sulphur in a current of coal-gas, and weighed as cuprous sulphide. The sulphur used should be recrystallised from carbon disulphide.



**The Estimation of Zinc.**—The filtrate from the copper sulphide is boiled to remove the last traces of sulphuretted hydrogen and rendered neutral with ammonia, then proceed as in **41**, p. 191.

*Notes.*—(1.) Stannic oxide is precipitated by the foregoing treatment in a state of purity, but it may contain iron, and possibly copper and lead, in small quantities. Should the stannic oxide from its colour show signs of impurity, it may be treated in the following manner :—Mix it in the crucible with 3 parts of dry sodium carbonate and 3 parts of sulphur, cover the crucible and heat it until the contents have completely fused and the excess of sulphur is volatilised. The mass is allowed to cool, and treated with water, which dissolves the stannic sulphide as sodium sulpho-stannate. Iron, copper, and lead will remain as sulphides. The former may become dissolved and give the solution a dark-green colour; in order to precipitate this, add a little ammonium chloride, and digest until the solution has turned yellow. Filter off the sulphides and wash with the usual precautions with sulphuretted hydrogen water; as small a filter as possible should be used. Wash the precipitates into a small porcelain evaporating

dish, add strong nitric acid, and dissolve by application of heat; cupric and ferric nitrates may be formed, and lead sulphate. Add some dilute sulphuric acid drop by drop to precipitate all the lead, filter off, dry, ignite, and weigh as  $\text{PbSO}_4$ . Calculate as  $\text{PbO}$  and deduct from the  $\text{SnO}_2$ . Then calculate as  $\text{Pb}$ . The filtrate from the lead sulphate is treated with ammonia in excess, the precipitate filtered off and dissolved in hydrochloric acid; it is then again precipitated by ammonia, washed, dried, and ignited. This is weighed as  $\text{Fe}_2\text{O}_3$ ; its weight must be deducted from the  $\text{SnO}_2$ . It must then be calculated as  $\text{Fe}$ . Should there be any copper present the blue colour of the ammoniacal filtrate will make this known. Acidify very carefully with hydrochloric acid, heat the solution in a porcelain basin till it commences to boil, add a dilute solution of pure caustic alkali till there is no further precipitation, keep the mixture near its boiling-point for a few minutes, and allow the precipitate to subside. Filter off the liquid, wash the precipitate two or three times by decantation, boiling up after each addition of water, collect the precipitate on the filter, wash thoroughly with hot water, dry, and ignite intensely. Add a single drop

of nitric acid, digest on the water-bath, add a particle of ammonium carbonate, and heat gradually to strong redness. Weigh as  $\text{CuO}$ . Deduct from the weight of the  $\text{SnO}_2$  and calculate as Cu.

- (2.) Lead sulphate is slightly soluble in pure water, but its solubility is decreased by acidifying the water with sulphuric acid. Thus : 1 part of lead sulphate dissolves in 22,800 parts of pure water and in 36,000 parts of water containing sulphuric acid. It is almost perfectly insoluble in alcohol or spirit of wine.
- (3.) Washing the filter with alcohol to remove the sulphuric acid is necessary, otherwise the filter would char or become brittle and fall to pieces.

*Example.*—A halfpenny was reduced to filings, and the following numbers were obtained in two analyses :—

	I.	II.
	Per cent.	Per cent.
Lead .	0·19	0·06
Tin .	4·38	3·96
Copper	93·96	94·47
Zinc .	1·66	1·56
	<hr/>	<hr/>
	100·19	100·05
	<hr/>	<hr/>

#### 40. ZINC BLENDE.

**Zinc Blende**, or "**Black Jack**," consists essentially of zinc sulphide, but it is very commonly mixed with other sulphides, especially with galena or lead sulphide, with iron, manganese, copper, and cadmium sulphides, and with calamine or zinc carbonate. The quartz or gangue, which contains no reducible metal, must be estimated.

The ore is reduced to the finest powder and carefully sifted. It is dried at  $100^{\circ}$  C. The sulphur and the metals are estimated in separate portions.

**Sulphur.**—(a) Weigh about 1 gram of the very finely powdered mineral into a pint beaker, add 50 c.c. of a strong solution of pure caustic potash or soda (perfectly free from sulphate), digest on the water-bath for an hour, or as much longer as may be convenient, add 100 c.c. of water, and then pass a slow current of chlorine into the liquid. The sulphur is thus oxidised to sulphuric acid, which remains in solution as an alkaline sulphate. Filter, acidify the alkaline filtrate with hydrochloric acid, but carefully avoid adding any great excess. The clear solution is now boiled. Weigh roughly 2.5 grams of barium chloride, dissolve it in boiling water, and add the hot solution at once to the beaker. Barium sulphate is immediately precipitated,

which settles down very rapidly. The liquid should be filtered while hot, the clear liquid being *decanted* from the granular precipitate. A washing bottle containing boiling water should be ready, and sufficient for a good washing be immediately poured upon the precipitate; a drop or two of dilute hydrochloric acid is added, the liquid is boiled for a few moments, and decanted on to the filter after standing for about two minutes. The addition of boiling water, but without hydrochloric acid, and then boiling and decanting, is repeated two or three times. The precipitate is then transferred to the filter, washed a few times, the filtrate tested until found to be neutral, and to give no residue when a drop is evaporated on a watch-glass. The precipitate is dried, removed from the paper to the platinum crucible, the filter burnt separately on a platinum wire, the whole ignited, the crucible being inclined, allowed to cool in a desiccator, and weighed (see 9, *Notes* (2) and (3), p. 55). Calculate as S.

*Notes.*—(1.) Unless the substance be reduced to a very fine powder, particles of quartz, pyrites, or cupric oxide may cause a tumultuous evolution of oxygen when chlorine is passed into the alkaline solution. This will occur by reason of the hypochlorite at first formed being decomposed. Such a reaction would prevent the complete oxidation of the sulphur.

- (2.) Most of the metals are precipitated as oxides, lead as peroxide, and if iron be present it is thrown down as ferric hydrate. If the passage of the stream of chlorine is continued too long, the formation of potassium ferrate is indicated by the liquid acquiring a red tint. The liquid is removed from the chlorine apparatus and gently heated with powdered quartz until the ferrate is decomposed.
- (3.) Though the sulphur is generally in combination with the metals as *sulphides*, sometimes *sulphates* are also present, and these should be estimated separately and reckoned as such by treating the mineral with hydrochloric acid, evaporating to dryness and filtering from gangue and silica. The sulphuric acid is estimated in the filtrate in the manner directed in 9, p. 51, and calculated as  $\text{SO}_3$ . The metal in combination must be reckoned as oxide.

**Extraction of Sulphur by Fusion.**—(b) This method is applicable only when no lead is present. The mineral, finely powdered, is mixed with about 6 parts of pure sodium carbonate, free from sulphate more particularly, and 4 parts of potassium nitrate, in a porcelain crucible. Heat is applied very gently at first, and finally raised to fusion over a blast-lamp,

and maintained at this high temperature for some time. The fused mass is allowed to cool slowly, extracted with water, filtered, and the residue washed with hot water. The filtrate may be suitably diluted, acidified with hydrochloric acid, and boiled. The sulphuric acid is precipitated from the hot solution by the method and in the manner already described (see 9, p. 51). Calculate as S.

**Estimation of the Metals.**—About 2 grams of the finely powdered mineral are placed in a fairly capacious beaker covered with a dial-glass. A conical beaker-flask, closed with a funnel, answers best. If there are carbonates present a little water may be added, and then gradually 5 c.c. fuming hydrochloric acid is poured from a measure. When all effervescence has ceased, add most of the remainder, about 20 c.c. of the hydrochloric acid, place on a sand-bath, and continue to heat as long as sulphuretted hydrogen is evolved. Finally, concentrate the liquid, and add fuming hydrochloric acid with four times its volume of nitric acid (sp. gr. 1.4), about 20 c.c. altogether; the flask is transferred to the water-bath, which must be placed in a good draught chamber. The whole is now evaporated to dryness on the water-bath, or at a low temperature on a sand-bath, strong hydrochloric acid is added to moisten the salts, and evaporation is again employed in order to decompose the nitric acid. Now add 5 c.c. of pure concentrated oil of vitriol (sp. gr. 1.80) diluted with

10 c.c. of water, and heat on a sand-bath until the hydrochloric and nitric acid are expelled. This volume should contain 8.64 grams of  $\text{H}_2\text{SO}_4$ . Dilute to 50 c.c. and filter. Wash the residue with water containing a little sulphuric acid, and then with purified methylated spirit, collecting the spirituous washings separately. The washed residue is dried, separated from the filter, transferred to a porcelain crucible, the filter burnt, and the whole weighed. This portion consists of silica, gangue undecomposed by acids, and lead sulphate. Heat the residue in a small beaker or in the crucible itself if it be large enough, with a solution of ammonium acetate and caustic ammonia, filter by decantation through a very small filter, repeat the process three or four times till nothing further is extracted, dry the filter, burn it in the crucible, and weigh again. The loss is lead sulphate.

**Estimation of Copper.**—Mix the solution of the sulphates with hydrochloric acid of sp. gr. 1.1, adding 40 c.c. to every 100 c.c. of liquid. Pass sulphuretted hydrogen into the liquid largely in excess of saturation, filter before the excess of the gas has had time to escape or become decomposed, keep the funnel covered with a glass plate, wash with hydrochloric acid saturated with sulphuretted hydrogen, then wash with sulphuretted hydrogen water. If the quantity of copper is small, dry, and ignite with the filter in a porcelain



crucible, mix with a little pure sulphur, and heat in a current of hydrogen or coal-gas in the covered crucible. Cool and weigh as  $\text{Cu}_2\text{S}$ . In every case after the first filtration sulphuretted hydrogen should be again passed through the liquid in order to see whether any further precipitation may occur.

**Estimation of Iron and Zinc.**—(c) The filtrate from the precipitate of copper sulphide is boiled in a wide-mouthed flask for a long time to expel sulphuretted hydrogen and as much hydrochloric acid as can be removed by this process. A flask with a round bottom, placed so that the neck is inclined at an angle of  $45^\circ$ , answers this purpose best. Before proceeding further, first convert the salts into acetates by removing all the sulphuric acid by means of barium acetate. Take 20 to 21 grams of dried pure barium carbonate and dissolve in acetic acid—an excess of acid is of no consequence—boil this solution and add it to the boiling liquid containing zinc and iron. The quantity actually necessary to precipitate 8.64 grams of  $\text{H}_2\text{SO}_4$  is  $20.14 \text{ BaCO}_3$ . Filter off the barium sulphate on a folded filter and add ammonium acetate in excess to convert all the chlorides into acetates, add acetic acid until a strongly acid reaction is observed with litmus-paper. Allow to cool, and pass a current of sulphuretted hydrogen through the liquid. Zinc is thus precipitated as sulphide. During filtration the funnel should be covered with a glass

plate in order to prevent too free access of air. The precipitate is washed with sulphuretted hydrogen water, dried on the filter, transferred to a porcelain crucible, the filter burnt on a platinum wire, the ash added to the crucible, and the whole sprinkled with powdered sulphur. The crucible is covered, a moderate stream of dry hydrogen or coal-gas is passed through, and a gentle heat applied; after a short interval the temperature is raised to redness; finally the lamp is removed, the current of gas is continued until the crucible is cooled; it is transferred then to a desiccator, and subsequently weighed as  $\text{ZnS}$ .

The filtrate is boiled with sufficient bromine water to peroxidise the iron, allowed to cool, neutralised with ammonium carbonate until of a deep red colour from the production of a basic ferric salt in the solution, boiled, and filtered hot. The filtrate should be colourless; but if iron remains in solution allow the liquid to cool, add a little more ammonium carbonate till nearly neutral, boil again, and filter. The precipitate is dried, ignited, and weighed as  $\text{Fe}_2\text{O}_3$ .

If manganese be present it may be precipitated as manganic hydrate by boiling with about 2 c.c. of bromine and adding an excess of strong ammonia. Allow to stand for an hour, digest on the water-bath, finally boil and filter. Burn the dried precipitate and filter in a platinum or porcelain crucible, and weigh as  $\text{Mn}_3\text{O}_4$ .

## ANOTHER METHOD FOR ESTIMATING IRON AND ZINC.

**Iron.**—(*d*) Take the filtrate from the copper sulphide, boil off the sulphuretted hydrogen, add a few drops of nitric acid or of bromine water, and boil to peroxidise the iron. The liquid is strongly acid ; therefore neutralise with ammonium carbonate until a reddish-brown precipitate begins to make its appearance, and the liquid exhibits a brownish-red colour. To this warm solution a perfectly neutral solution of ammonium succinate is added, which throws down the iron as a ferric succinate ; a gentle heat is then applied, and the liquid allowed to cool. When perfectly cold the solution is filtered and the precipitate washed with cold water and afterwards with ammoniacal water to free it from a portion of the succinic acid. This imparts a darker colour to the precipitate. The precipitate is then dried, transferred to a crucible, the filter-paper added, ignited, cooled, and weighed as  $\text{Fe}_2\text{O}_3$ .

**Zinc.**—(*e*) The filtrate containing the zinc is fairly diluted with water so as to make up a volume approaching a litre. No ammonium chloride need be added, since the neutralisation of the strongly acid solution with ammonium carbonate has yielded abundance. Ammonia is added until the liquid is alkaline ; it is then boiled, and the zinc precipitated with sulphide of ammonium, which must not be more than slightly yellow.

Old preparations containing much ammonium polysulphide should not be used. The ammonium sulphide should be added in no greater excess than is necessary to just precipitate the whole of the zinc as  $\text{ZnS}$ . Continued boiling causes the precipitate to become granular, and so renders it easy to filter. When the flask has been allowed to stand in a warm place till the zinc sulphide has settled, some of the clear supernatant liquid is tested with ammonium sulphide. The liquid should be filtered while hot, for in this way filtration is much facilitated. The washing is carried out with a dilute solution of ammonium sulphide and chloride, observing the precautions already mentioned (38, p. 168).

Treat as directed on p. 186, and weigh as  $\text{ZnS}$ .

*Example.*—Blende containing no lead was treated by fusion for sulphur.

Taken for the estimation of sulphur, 0.2577 grams.

„ „ of metals, 1.0582 „

	Per cent.
Zinc .	59.662
Sulphur	31.682
Silica .	5.859
Copper	0.090
Iron .	2.665

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99.958

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## 41. GALENA.

This mineral is essentially lead sulphide, but it contains more or less iron, copper, silver, and less frequently antimony. Blende is also associated with galena. More or less gangue insoluble in acids is present.

The analysis is conducted differently, according to the absence or presence of antimony in the ore.

### GALENA FREE FROM ANTIMONY.

**Lead.**—Oxidise from 1 to 2 grams of the very finely powdered mineral with highly concentrated fuming nitric acid, free from chlorine and sulphuric acid, using for the purpose a large flask covered with a watch-glass. If the acid is of sufficient strength all the sulphur will be oxidised to sulphuric acid. Warm gently for a long time, and add 3 or 4 c.c. of pure oil of vitriol previously diluted with 12 c.c. of water, and heat on asbestos cardboard or a sand-bath till all the nitric acid has been expelled. Dilute, filter, and wash the residue with water containing sulphuric acid, and finally displace this with alcohol, taking care that the alcoholic washings do not run into the main portion of the filtrate. Dry the residue on the filter, ignite, and weigh. Previous to ignition in a *porcelain crucible*, the precipitate must

be carefully removed from the filter-paper and transferred to the crucible; cover it and ignite strongly *with only the tip of the flame* of a *Bunsen burner*. Wrap the filter-paper with the soiled portion inside, bind it up with platinum wire and burn, letting the ash fall on to the inverted lid of the crucible; treat the ash with a drop of strong nitric acid and warm, add a drop of sulphuric acid, heat more strongly, finally ignite and weigh. These precautions are intended to prevent the reduction of any of the lead sulphate by the gases from the burner or by the filter-paper.

**Gangue.**—Remove the lead sulphate from the crucible to a beaker, and pour upon it some ammonium acetate rendered strongly alkaline with ammonia, and warm.

Decant the solution of lead sulphate in ammonium acetate on to a filter, and treat the residue again until nothing further is extracted, wash with water, then dry, ignite, and weigh the residue. The first weight *minus* the second gives the lead as sulphate. Calculate the lead as Pb.

**Silver.**—The filtrate, which contains sulphuric acid and metals such as silver, copper, iron, and zinc, now separated from the lead, is treated as follows:—

Add a little hydrochloric acid to precipitate silver if present, keep the liquid in a warm place for some two or three hours for the silver chloride to collect. Filter

through a small filter, and wash the silver chloride with water acidulated with nitric acid, afterwards with pure water. Dry and transfer the precipitate to a small porcelain crucible; gently ignite till the silver chloride commences to fuse, and burn the filter-paper. Touch the ash, which is either in the crucible or on the inside of the lid, with a drop of nitric acid, warm, add a drop of hydrochloric acid, gently heat to drive off the water, gently ignite and weigh as  $\text{AgCl}$ . Calculate as  $\text{Ag}$ .

**Copper.**—The filtrate after separation of the silver is precipitated by a stream of sulphuretted hydrogen, the copper sulphide filtered off and washed with sulphuretted hydrogen water, then dried, transferred to a crucible, the filter burnt, and the copper sulphide heated with sulphur in a current of coal-gas and weighed as  $\text{Cu}_2\text{S}$ .

**Iron.**—The filtrate from the copper is boiled to expel the last traces of sulphuretted hydrogen, and concentrated by evaporation. Oxidise by boiling with a drop or two of nitric acid, add ammonium chloride rather freely, and precipitate ferric hydrate and alumina with excess of ammonia. Dissolve the precipitate in hydrochloric acid, and once more treat in the same way. Filter, and if the precipitate is small, moisten the filter with a saturated solution of ammonium nitrate, ignite the filter and precipitate together in a crucible. Calculate as  $\text{Fe}$ .

**Zinc.**—The alkaline filtrate from the iron and alumina

is rendered neutral by the proper addition of hydrochloric acid or acetic acid, and then boiled. To the boiling liquid ammonium sulphide is added, a large excess being avoided. The liquid is again boiled for twenty minutes; the precipitate thus becomes granular and settles down readily. The clear liquid is to be treated with a drop of ammonium sulphide to make sure of the complete separation of the zinc, and the sulphide is washed with hot water. The washing is easily and rapidly performed. The zinc sulphide is next partially dried in the filter, transferred to a porcelain crucible and ignited, at first gently and afterwards strongly with free access of air. The expulsion of the last traces of sulphur as sulphur dioxide is much facilitated by dropping fragments of ammonium carbonate into the crucible. Pure zinc oxide remains, which should be ignited until its weight is constant.

Or, instead of prolonged igniting, by which the  $\text{ZnS}$  is converted into  $\text{ZnSO}_4$  and afterwards decomposed, leaving a residue of  $\text{ZnO}$ , the zinc sulphide may be mixed with sulphur, heated in a current of a coal-gas, and weighed as  $\text{ZnS}$  (40, p. 186). Calculate as Zn.

**Sulphur.**—For the estimation of sulphur a separate portion of the mineral is weighed out and treated according to the method generally applicable to sulphides (40, p. 180).



## GALENA CONTAINING ANTIMONY.

About 1 gram of the mineral reduced to the finest powder is dissolved by heating in an evaporating basin with strong hydrochloric acid, the liquid being prevented from loss by an inverted funnel, which allows of the escape of sulphuretted hydrogen only.

After complete solution of the sulphide the liquid is decanted into a beaker, boiled with water, and filtered while hot to prevent the separation of crystals of lead chloride. The residue in the evaporating dish is then boiled with water and decanted on to a filter; this is repeated if necessary; finally, everything is transferred to the filter and washed with boiling water till no lead can be detected in the filtrate. The small residue is burnt with the filter in a crucible and weighed.

**Lead.**—The filtered liquid is warmed to retain all the lead chloride in solution, and the greater part of the lead is precipitated by the addition of sulphuric acid, and put aside to settle. The liquid is decanted through a filter, the lead sulphate is filtered and washed with water somewhat strongly acidified with sulphuric acid. Then proceed as directed on p. 189.

The acid and aqueous portions of the filtrate, which contain lead, antimony, zinc, and iron as chlorides and sulphates, are treated with sulphuretted hydrogen and filtered. Dilute a small portion of the filtrate with

an equal volume of water, and again pass the gas through it. If there be a further precipitation, treat the whole of the filtrate in the same way. Wash with water twice or thrice, and filter off the lead and antimony sulphides; wash them into a beaker or evaporating basin, and digest with yellow ammonium sulphide on the water-bath for some time, the beaker or dish being covered with a glass plate. Pour off the liquid and digest the residue again. Filter—the filtrate contains the antimony.

**Antimony.**—The solution is mixed with an excess of dilute hydrochloric acid and boiled for twenty minutes, while a current of sulphuretted hydrogen is passed through the liquid; the precipitate is filtered off, some tartaric acid is dissolved in the liquid, and, after a further addition of water, the liquid is boiled again, the gas being passed through continuously. By this treatment the voluminous antimony sulphide becomes a dense granular powder, without suffering loss. In this condition it can be filtered and washed with great facility. It is transferred to a porcelain crucible, the filter burnt and added thereto; one or two crystals of sulphur are put on to the precipitate, and it is ignited in a current of coal-gas and weighed as  $\text{Sb}_2\text{S}_3$ .

**Iron and Zinc.**—These metals are separated in the manner already described (41, p. 191) from the filtrate which ran from the precipitate of lead and antimony sulphides.

*Note.*—If copper be present, the digestion of the sulphuretted hydrogen precipitate must be made with sodium sulphide containing some dissolved sulphur instead of with ammonium sulphide, since this latter dissolves small quantities of copper sulphide.

## 42. SILICATES.

Siliceous minerals are generally termed soluble or insoluble silicates, according as they are dissolved or not by treatment with strong hydrochloric acid.

**Soluble Silicates.**—Such silicates as are soluble in acids, and some which dissolve even in water, are susceptible of very simple treatment in order to separate the silicic acid and convert the bases into chlorides.

It suffices to acidify a solution with hydrochloric acid, evaporate down to dryness in a porcelain dish upon the water-bath, and treat two or three times with water and acid, on each occasion *evaporating to dryness*.

The soluble silicic acid is then converted into an insoluble modification. It may be separated from the bases which have been converted into chlorides by dissolving in water and filtering off the silica.

It is always necessary to test the *purity of the silica* by ascertaining its solubility in a concentrated hot solution of sodium carbonate.

**Insoluble Silicates.**—The silicates of the alkalis form a glass which is soluble in water and in dilute acids. By fusion with alkaline carbonates an insoluble may be converted into a soluble silicate, and the above treatment may be applied to it. This method is very generally applicable for the separation and estimation of silica, and all bases excepting the alkalis. The separation of alkalis must be the subject of a distinct process.

These processes may be enumerated as follows :—

- (a) Treatment with lime and calcium chloride, which result from the decomposition, in presence of the mineral, of calcium carbonate and ammonium chloride at a high temperature.
- (b) Treatment with an aqueous solution of hydrofluoric acid and sulphuric acid. It is necessary to employ a very strong solution of hydrofluoric acid.
- (c) Treatment with gaseous hydrofluoric acid in a leaden box, the mineral being finely powdered and moistened with dilute sulphuric acid.
- (d) Fusion with barium hydrate at a high temperature or barium carbonate, or with a mixture of barium carbonate and barium chloride.
- (e) Sintering or incipient fusion of the mineral with bismuth oxide.

It is obvious that the treatment with hydrofluoric acid is advantageous in admitting of all the bases being estimated in one weighed sample of the mineral; but highly aluminous minerals, such as, for instance, kyanite, are not easily attacked.

### THE SELECTION OF SPECIMENS.

Very definite and homogeneous specimens should be taken for analysis. Selected crystals are to be preferred, from which all gangue or matrix has been picked. They should, as far as possible, be not only similar in form but in colour, transparency or translucency, and hardness. Crystals which have "weathered" may have quite a different composition. If small, the sorting of crystals may be much facilitated by the use of a pair of forceps and a good magnifying lens.

The following substances may be taken for analysis:—

**Glass.**—Crown glass. Flint glass.

**Felspars**—

Orthoclase,  $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot \text{K}_2\text{O} \cdot 3\text{SiO}_2$ .

Albite,  $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot \text{Na}_2\text{O} \cdot 3\text{SiO}_2$ .

Petalite,  $4\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{Na}_2\text{O} \cdot 2\text{Li}_2\text{O} \cdot 6\text{SiO}_2$ .

**Garnets** of variable composition represented by the formula  $6\text{R}''\text{O} \cdot 3\text{SiO}_2 \cdot 2\text{R}'''\text{O}_3 \cdot 3\text{SiO}_2$ ; where  $\text{R}'' = \text{Mg, Ca, or Fe}''$ , and  $\text{R}''' = \text{Al}''', \text{Fe}''' \text{ or } \text{Cr}'''$ .  $\text{R}_2\text{O}_3$  is generally alumina.

**Beryl.**— $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ .

**Estimation of Water.**—The mineral is pulverised, and without loss of time transferred to a weighed platinum crucible, covered, weighed again, and ignited for five minutes. When there is no risk of loss from decrepitation or violent expulsion of water-vapour, the crucible is uncovered and inclined, heated again, allowed to cool, and weighed, the operation being repeated until the weight is proved to be constant; the loss of weight is due to expelled water. After drying in the manner described the mineral may be further reduced to an impalpable powder by trituration in an agate mortar, carefully sifting, and tritulating again; it may then be transferred to a tube, from which a portion is to be taken for further examination.

**Fusion.**—About 1 gram is weighed in a platinum crucible and most intimately mixed with not less than 6 grams of equal proportions of perfectly pure anhydrous potassium and sodium carbonates. The mineral is mixed by stirring, with a rounded glass-rod, small portions of the carbonates which are added to the crucible from a weighed portion contained in a watch-glass or on a card. Before adding the last portion the glass rod is tapped gently on the side of the crucible to detach adhering particles, and wiped upon the carbonate which remains, which is then put into the crucible. It is necessary before heating to bear in mind that much carbon dioxide

will escape, and that this may cause loss by spiriting unless the following precautions are taken. The crucible must be large enough to hold at least two or three times the material to be heated. The heat applied at first must be moderate. The crucible must be covered, and the lid must be easily removable, in order that the progress of the fusion may be watched. As soon as it is seen that the mineral and the carbonates have commenced to react, and that a semi-fusion has occurred, the temperature must be greatly increased until a tranquil fusion results. The crucible must be placed on a triangle of stout platinum wire, capable of bearing the weight of the crucible at the highest temperature without bending sufficiently to allow of it falling through, or it may be placed on a clay triangle, which is perfectly sound and not likely to give way. The heating is effected by means of a blast-lamp or gas blow-pipe. The fusion ended, remove the crucible with tongs and place it while red-hot on a massive piece of polished iron, such as an anvil or the smooth surface of a large flat iron. The crucible is thus chilled, and the glass within separates easily from the metal. The fused mass, if it has come clean away from the platinum, is placed in a beaker of 250 c.c. capacity and about 100 c.c. of water are poured into it. If anything has adhered to the inside, the crucible may itself be transferred to the beaker. The beaker must be covered with a clock-glass,

the concave side downwards, and then little by little hydrochloric acid may be added to the covered beaker ; when all effervescence has ceased and an excess of acid has been added, the drops of moisture on the clock-glass must be rinsed into the beaker. The crucible should be removed to an evaporating basin thoroughly rinsed with dilute hydrochloric acid, and the rinsings added to the beaker ; it may then be washed with the washing bottle and the washings added thereto.

The beaker is heated on the water-bath for some time in order to free the liquid from carbonic acid and dissolve all the chlorides which have been formed. At this stage one can generally tell whether the fusion has been successful, for if there are any particles of the mineral remaining undecomposed they will be detected by the gritty feeling when a rounded glass rod is drawn across the bottom of the beaker.

**Separation of the Silica.**—The solution mixed with silica which has separated is evaporated to dryness on the water-bath in a porcelain dish about 5 inches in diameter. When much of the acid has been expelled and the contents of the dish are in a pasty condition, they should be carefully stirred with a rounded glass-rod—lumps should be broken up ; a little boiling water may be added to moisten the salts, and the evaporation after this addition is carried to complete dryness. Should there be a difficulty in attaining perfect dryness on the



water-bath, the dish is transferred to a tripod stand at least a foot in height, and heated gently by means of a flat gas burner giving a number of small and low flames spread over a large surface. In this manner the salts cannot easily be overheated. On no account heat over an ordinary Bunsen, for if the porcelain dish be overheated at any point the silica might recombine with some of the bases from which it has been separated. After evaporation to dryness allow the dish to cool, and moisten the contents with hydrochloric acid, so that the mixture is pasty, then add a little more acid, allow it to stand for half an hour, heat on the water-bath, add hot water, stir, place aside until the silica has deposited, and decant the solution on to a filter. Repeat the process a second and a third time, and continue as long as the washings show any turbidity with silver nitrate solution, transfer the silica to the filter, wash well with hot water. Thoroughly dry the silica on the filter, transfer it to a weighed platinum crucible, and ignite as strongly as possible until nothing but white silica is left.

To test the *purity of the silica* it should be heated on the water-bath in a silver dish with 50 c.c. of a saturated solution of sodium carbonate and 80 c.c. of water. The solution should be filtered hot, and the operation should be repeated. If all does not dissolve, the clear solution is decanted on to a filter and the residue treated with a little more sodium carbonate, and then the liquid and

residue are transferred to an ashless filter. It is thoroughly washed, dried, ignited, and weighed.

If the siliceous residue is gritty and like minute grains of sand, the mineral has not been sufficiently finely powdered; the residue should then be reduced to a more finely divided state, and a second fusion made.

If it be in a very fine powder it may be fused again with six times its weight of the mixed carbonates, proceeding as before. The two fusions should, if possible, be analysed separately, for it remains to be seen whether they are derived from the same or from two different minerals.

**Separation of the Bases.**—The entire filtrate and washings from the silica are boiled, and a current of sulphuretted hydrogen is passed through the solution until cold. Metals such as lead and copper are thus precipitated, and are separated by filtration. In such a manner lead is separated in the analysis of flint glass, and copper from garnets.

**Lead** may be estimated by oxidising the sulphide with nitric acid, converting it entirely into sulphate by addition of sulphuric acid, and proceeding as directed on p. 189. Calculate as  $\text{PbO}$ .

**Copper** may be estimated in the filtrate from the lead sulphate by precipitating with sulphuretted hydrogen, and after ignition mixing the precipitate with sulphur and igniting in a current of coal-gas, the

cuprous sulphide being weighed and regarded as  $\text{CuO}$  (see 38, p. 169, and 41, p. 191).

**Separation of Iron and Alumina.**—The filtrate and washings after the separation of the sulphides, or where no metals precipitable by sulphuretted hydrogen are present after filtration from the silica, are boiled for a time, and then a few drops of nitric acid are added to peroxidise the iron salt. Add ammonium chloride and ammonia in slight excess, boil the liquid a second time, allow it to stand till clear, decant, filter off the precipitate, and wash it well with hot water. In order to purify the ferric hydrate from lime and magnesia, the precipitate is redissolved and reprecipitated in the same way. After again filtering, the first and second filtrates are mixed and put aside for the estimation of calcium and magnesium. To estimate the iron, hydrochloric acid is poured upon the filter, a silver dish is put below the funnel, a hole is made in the apex of the filter with a glass rod, and all traces of the precipitate are washed into the dish. The filter is then again moistened with acid, and thoroughly washed with water. A concentrated solution of perfectly pure caustic potash or caustic soda (free from silica and alumina) is added to the filtered liquid in large excess and boiled. The iron separates a ferric hydrate, while the alumina goes into solution as an alkaline aluminate. The precipitate formed is filtered off, washed thoroughly with boiling distilled water, and,

in order to purify the ferric hydrate from alkali, redissolved in hydrochloric acid and reprecipitated by addition of an excess of ammonia and subsequent boiling. The precipitate is filtered, washed with boiling water, dried, ignited, and weighed as  $\text{Fe}_2\text{O}_3$ . The iron must be calculated as  $\text{FeO}$  or  $\text{Fe}_2\text{O}_3$ , according to whether the presence of ferrous or ferric oxide has been proved by the qualitative examination.

**Estimation of Alumina.**—Boil the moderately dilute solution of alumina in the dish, and add some perfectly pure crystallised ammonium chloride ; boil, and add more of the salt until ammonia gas is no longer evolved in sufficient quantity to cause turmeric paper to become brown. The liquid is allowed to stand until it can be decanted from the precipitate. It is then poured on to a filter, the precipitate washed with boiling water, stirred, allowed to settle, decanted, and so treated for a third and fourth time. Filter, wash, dry, ignite, and weigh as  $\text{Al}_2\text{O}_3$ .

**Calcium and Magnesium.**—The filtrate from the precipitate produced with ammonium chloride and ammonia is concentrated by evaporation ; to the hot solution add ammonium oxalate in excess, subsequently a few drops of ammonia are added ; the beaker-glass is covered and set aside in a warm place until next day, when it will be found that the precipitate of calcium oxalate has subsided. Cautiously decant the liquid so

as to leave the precipitate undisturbed, wash the precipitate two or three times by decantation with hot water, and rinse the precipitate into the filter with small quantities of hot water, waiting until all the liquid has passed through the filter on each occasion before adding more water. Small particles of oxalate adhering to the glass may be removed by a feather or a glass rod tipped with india-rubber tubing. Should it prove impossible to remove all the precipitate in this manner, a few drops of very dilute hydrochloric acid are brought over every part of the beaker with a glass rod ; when all is dissolved ammonia is added to the solution, in order to reprecipitate the oxalate.

Before proceeding to filter this solution remove from beneath the funnel the beaker containing the filtrate and put another beaker in its place. The small quantity of oxalate may now be transferred to the filter. Wash with warm water until 1 c.c. of the liquid gives no precipitate with calcium chloride. Dry the precipitate in the funnel, remove the filter, detach the precipitate as completely as possible, and transfer it to a weighed platinum crucible. The filter is folded up, wrapped round with platinum wire, and burnt over the crucible, into which the ash is allowed to fall. The ash must not be allowed to mix with the calcium oxalate. The operation may now be varied, according to whether the lime is very small in

amount or fairly large. If small, heat intensely over a blast-lamp until no trace of greyness caused by carbon is observed within the crucible, cover with the lid, and weigh as caustic lime. Repeat this until a constant weight is obtained.

When the calcium oxalate is sufficiently large in amount to make a distinct layer over the bottom of the crucible about one or two millimetres in depth, burn the precipitate over a lamp until every trace of carbon of the filter-ash is consumed. This should convert the calcium oxalate into carbonate, and if the operation be very carefully conducted, a change will be observed in the precipitate amounting to a slight greyness in colour; only a moderate red-heat is necessary. If the heat has been too strong at any point the calcium carbonate will have been converted into caustic lime, and to ascertain whether this is so, the crucible had better be weighed after cooling in a desiccator and the precipitate tested as follows. Add a drop of water to the precipitate, and test whether it has an alkaline reaction by touching it with a minute slip of turmeric or red litmus paper. If the paper becomes brown or blue, rinse it with a drop or two of water, add a little powdered ammonium carbonate, and evaporate on the water-bath to dryness. Heat the crucible once more, at first gently, then for five to ten minutes more strongly and uniformly, so that a dull redness is

seen at the outside of the crucible. This may best be done by an Argand or Bunsen-Argand burner. If an ordinary Bunsen be used it should be moved with the hand, so that the flame is prevented from playing long upon one place. Weigh after cooling in a desiccator. The operation should be repeated until the weight is constant. The substance is calcium carbonate.

**Estimation of Magnesium.**—The filtrate from calcium oxalate is concentrated, cooled, and mixed with an excess of ammonia. Sodium phosphate is added to the cold solution; it is then stirred well with a glass rod, which is not allowed to touch or strike the sides of the beaker, and the liquid is set aside for twelve hours. The clear liquid is decanted on to a filter and allowed to run through before the precipitate is washed on to the filter with dilute ammonia.<sup>1</sup> It is advisable to proceed very carefully with the washing of the precipitate, not adding too much liquid at a time, and allowing this to run away completely before adding a further quantity. When silver nitrate ceases to give a precipitate if added to 1 c.c. of the liquid acidified with nitric acid, the washing may be discontinued and the precipitate dried. The dried precipitate detached from the filter is transferred to a platinum crucible, which is covered and heated very gently for some time; finally the temperature is in-

<sup>1</sup> One volume ammonia, sp. gr. 0.96, and three volumes of water.

creased to bright redness on the blast-lamp. The filter is burnt on platinum wire and the ash added to the contents of the crucible; heat is then applied until the ash is quite white. Cool in a desiccator and weigh as  $\text{Mg}_2\text{P}_2\text{O}_7$ .

**Alkalies.**—About  $1\frac{1}{2}$  grams of the mineral in an impalpable powder are mixed with  $1\frac{1}{2}$  grams of ammonium chloride and 9 grams of a special preparation of pure calcium carbonate. The mixture must be made in a platinum crucible with all the care observed in preparing for fusion with alkaline carbonates. The platinum crucible is imbedded in magnesia contained in a Hessian crucible, which is heated in a gas furnace for an hour. The fused mass is treated with water and boiled. The solution is filtered, the residue washed thoroughly, ammonium carbonate is added in excess, and the liquid is boiled. The precipitate is composed of magnesium and calcium carbonates; it is washed completely. The filtrate should be tested by adding a few drops of ammonium carbonate and allowing it to stand for some time; if there is no precipitate the liquid may be evaporated to dryness in a platinum basin and gently heated, *but not to redness*. Now dissolve the residue in water, rinse out the dish, and observe whether the solution is perfectly clear; if so, add a few drops of ammonia and ammonium carbonate; if a precipitate forms, filter the liquid into the platinum dish, and again evaporate and heat as before.



The residue is composed of alkaline chlorides ; the dish is cooled in a desiccator, covered with a film of mica, and weighed. It may then be gently heated again and the weighing repeated.

**Estimation of Potassium.**—The chlorides are next dissolved in water, transferred to a porcelain basin, and mixed with an excess of platinic chloride, containing 10 grams of platinum in 100 c.c. The solution is evaporated to a pasty condition on the water-bath, with frequent stirring, in order to get rid of as much free hydrochloric acid as possible. Pure methylated spirit of 95 per cent is added, the dish is covered with a glass plate or inverted funnel, and allowed to stand for a few hours with occasional stirring. If the liquid appears of a deep yellow colour, sufficient of the platinic chloride has been added to precipitate all the potassium. The clear and strongly yellow liquid is decanted on to an ashless filter (No. 589, see p. 11). The residue is washed with methylated spirit by decantation, and is then minutely examined with a lens. It should consist of small yellow octahedral crystals ; any admixture of white saline particles indicate the presence of sodium chloride which has escaped conversion into the platinic sodium chloride. In this event the precipitate must be treated with water till all the sodium chloride is dissolved, a further quantity of platinic chloride is added, the liquid is evaporated nearly to dryness, and the examination is repeated. The residue, consisting of

potassio-platinic chloride, is then washed as before, and transferred to a weighed porcelain crucible by means of a jet of alcohol from a small washing bottle; the alcohol is removed by evaporation on the water-bath.

The crucible containing the dried precipitate is now covered and heated very gently for a considerable time; gradually increase the temperature, and then allow the crucible to cool. Remove the lid, place the crucible on a plate, and holding the dried and folded filter-paper by a pair of steel forceps or crucible tongs, it is set on fire. The ash falls into the crucible; it is completely calcined, and then there is added a minute quantity of perfectly pure oxalic acid. The crucible is then covered and ignited, at first gently, afterwards more strongly. The oxalic acid greatly facilitates the decomposition of the potassio-platinic chloride. The contents of the crucible are now treated with water, and the residue of platinum is washed until the washings no longer cause a precipitate in a solution of silver nitrate.

The platinum is ignited and weighed.

An atom of platinum represents two atoms of potassium. Calculate as  $K_2O$ .

*Example—*

**Analysis of Garnets from Donegal.**—Separation and estimation of silica, lime, alumina, ferric oxide, and alkalis, with small quantities of cuprous oxide and magnesia.

Taken for analysis, 0.763 gram—

	Per cent.
Silica . . .	41.34
Lime . . .	32.28
Alumina . . .	18.86
Ferric oxide . . .	6.18
Cuprous oxide . . .	0.32
Magnesia . . .	0.12
Potash . . .	0.91
Soda . . .	0.72
	<hr/>
	100.73
	<hr/>

After the separation of the silica, the liquid acid with hydrochloric acid was precipitated by sulphuretted hydrogen. The small quantity of copper sulphide was weighed on a filter (p. 19), and calculated as  $\text{Cu}_2\text{O}$ .

#### PREPARATION OF PURE CALCIUM CARBONATE FOR THE DECOMPOSITION OF SILICATES.

Dissolve some good marble in commercial hydrochloric acid, and boil the solution with a little strong nitric acid, dilute with boiling water and render alkaline with ammonia. Boil again and filter. To the hot filtrate, which is largely diluted with boiling water, add ammonium carbonate in excess, allow to cool and settle. Decant the

liquid and wash by decantation in a large vessel several times with water.

By this treatment the powder is precipitated in a dense form, so that it occupies but a comparatively small space in the crucible; it is essentially pure calcium carbonate.

Pure recrystallised ammonium chloride should be used with the carbonate, and if the salt is not purchasable the ordinary salt should be specially recrystallised.

The reason for the action of a mixture of calcium carbonate and ammonium chloride upon silicates is the formation of a concentrated solution of caustic lime in fused calcium chloride, and the facility with which the caustic alkaline earth is thus caused to act upon the mineral.

Calcium carbonate and ammonium chloride of course, under mutual decomposition, form ammonium carbonate and calcium chloride. The action of heat fuses the chloride and converts another portion of calcium carbonate into caustic lime.

#### REMOVAL OF THE AMMONIUM SALTS WITHOUT IGNITION.

After the complete separation of the calcium by means of ammonium carbonate and oxalate, the ammonium salts may be removed from the filtrate by

boiling in a round-bottomed flask, the neck being inclined at an angle of  $45^\circ$ , and adding about 3 grams of nitric acid for every gram of ammonium chloride calculated to be present. The addition of acid should be made cautiously. When the evolution of nitrogen resulting from the decomposition of ammonia salts has ceased, the liquid, evaporated down to a small bulk in the flask, is treated repeatedly with strong hydrochloric acid in a porcelain evaporating basin to destroy the nitrates and convert the bases entirely into chlorides. After evaporation to dryness in a platinum basin once or twice with water, heating short of redness will render the chlorides fit to weigh. This treatment was employed in **Example 44**.

### 43. BERYL.

The analysis is performed in the manner already described for insoluble silicates, and the silica is separated as usual, then proceed as follows :—

**Estimation of Iron.**—The filtrate and washings from the silica are boiled with a few drops of nitric acid, a slight excess of ammonium chloride and ammonia are added, the liquid is boiled again, the precipitate filtered off and well washed. Hydrochloric acid is poured upon the filter, a silver dish is put below the funnel, a hole is made in the apex of the filter with a

glass rod, and all traces of the precipitate are washed into the dish. The filter is then again moistened with acid, and thoroughly washed with water. A concentrated solution of perfectly pure caustic soda or potash, free from silica and alumina, is added to the filtered liquid in large excess and boiled. The precipitate formed is filtered off, washed thoroughly with boiling water, redissolved in hydrochloric acid, and reprecipitated by adding an excess of ammonia and subsequent boiling.

The precipitate is filtered off, washed with boiling water, dried, ignited, and weighed as  $\text{Fe}_2\text{O}_3$ , but calculated as  $\text{FeO}$ .

**Estimation of Beryllia and Alumina.**—The solution in caustic alkali, which contains the two bases, is acidified with hydrochloric acid, boiled, treated with a slight excess of ammonia, and boiled again. The precipitate is filtered off, washed thoroughly with boiling water, and digested in a corked flask, without removal from the filter-paper, with a saturated solution of ammonium carbonate. After an interval of not less than twenty-four hours the portion of the precipitate which remains undissolved is filtered off, washed thoroughly, dried, burnt with the filter, and weighed as  $\text{Al}_2\text{O}_3$ . The solution of beryllia in ammonium carbonate is largely diluted with water and boiled in an evaporating dish for a long time—a basic beryllium carbonate sepa-

rates. The liquid and precipitate are transferred to a beaker, the solution is syphoned off when quite clear, and the remainder is poured on to a filter. The precipitate is washed, dried, burnt, and weighed as BeO.

For calcium, magnesium, and the alkalies, proceed as with other silicates.

*Note.*—Instead of treating the solution of beryllia and alumina with hydrochloric acid, and precipitating the former with ammonia and digesting with ammonium carbonate, the author finds that acidifying with acetic acid, and boiling, precipitates the alumina without carrying down any weighable quantity of beryllia. The beryllia may be precipitated from the filtrate by ammonia.

*Example.*—Radiated beryl from Glen Cullen, County Dublin. The composition of the mineral is in agreement with the following formula :—



This mineral requires at least six times its weight of mixed carbonates for its decomposition. Its composition apparently differs from ordinary beryl by  $\frac{1}{3}$ , the silica being replaced by alumina.

The fusion of 1 gram with 6 grams of mixed carbon-

ates left a slight residue of mineral unattacked, as shown by its insolubility in a solution of sodium carbonate. The separate fusion of the residue yielded a very decided green colour, characteristic of manganese.

### Analysis I.—

$$\text{SiO}_2\text{—1st weighing . . .} = 0.5518$$

$$\text{Undecomposed mineral . . .} = 0.1035$$

$$\text{SiO}_2\text{—2d weighing . . .} = 0.0264$$

Actual quantity of  $\text{SiO}_2$  present in 1 gram of substance—

$$= 0.5518 \text{ gram} - 0.1035 \text{ gram} + 0.0264 \text{ gram.}$$

$$= 0.4747 \text{ gram SiO}_2.$$

### Bases—

1st Fusion. 2d Fusion.

$$\text{CaO} = 0.0232 + 0.0028$$

$$\text{MgO} = 0.0041 + \text{a trace}$$

$$\text{Fe}_2\text{O}_3 = 0.0294 + 0.0055$$

$$\text{Al}_2\text{O}_3 = 0.2652 + 0.0657$$

$$\text{BeO} = 0.1092 + 0.0037$$

$$\text{Mg}_2\text{P}_2\text{O}_7 = 0.0144$$

$$\frac{80 \times 0.0144}{220.9} \overset{\text{MgO.}}{=} 0.00413$$

1st Fusion. 2d Fusion.

$$\text{Fe}_2\text{O}_3 = 0.0294 + 0.0055$$

$$= 0.0349$$

$$\text{Fe}_2\text{O}_3 = 160 \text{ and}$$

$$2\text{FeO} = 144$$

$$\frac{144 \times 0.0349}{160} \overset{\text{FeO.}}{=} 0.0314$$



**Alkaline Bases—**

	Grams.
Weight of substance taken . . .	= 1·5
Weight of mixed chlorides . . .	= 0·0277
Weight of platinum from $\text{PtK}_2\text{Cl}_6$ . . .	= 0·0196

Calculation to find the potash and soda in 1·5 grams of the mineral—

$\text{K}_2 = 78$	$\text{K} = 39$
$\text{O} = 16$	$\text{Cl} = 35\cdot5$
<hr/>	<hr/>
94	74·5
<hr/>	<hr/>
$\text{Pt} = 196\cdot7$	$2\text{KCl} = 149$

$$\frac{0\cdot0196 \times 94}{196\cdot7} = 0\cdot0093 \text{K}_2\text{O}$$

$$\frac{0\cdot0196 \times 149}{196\cdot7} = 0\cdot01485 \text{KCl}$$

$\text{Na} = 23$	$\text{Na}_2 = 46$
$\text{Cl} = 35\cdot5$	$\text{O} = 16$
<hr/>	<hr/>
58·5	62
<hr/>	<hr/>

$$2\text{NaCl} = 117$$

Mixed Chlorides.	KCl.	NaCl.
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$$0\cdot0277 - 0\cdot0148 = 0\cdot0129$$

$$\frac{62 \times 0\cdot0129}{117} = 0\cdot0068 \text{Na}_2\text{O}$$

Water expelled from 0.5 gram of the mineral = 0.0024 gram.

The statements of two different analyses show the necessity for selecting specimens. I. and II. were made from crystals which differed in this respect, that II. appeared to have "weathered" considerably.

	Specimen I. Per cent.	Specimen II. Per cent.
Silica . .	47.47	54.27
Alumina . .	32.49	27.23
Beryllia . .	11.29	10.50
Lime . .	2.60	1.40
Ferrous oxide	3.13	2.88
Magnesia . .	0.41	0.47
Soda . .	0.45	0.47
Potash . .	0.62	0.41
Water . .	0.48	...
	<hr/> 98.94 <hr/>	<hr/> 97.63 <hr/>

#### 44. PETALITE.

The estimation of silica, ferric oxide, alumina, lime, and magnesia is made according to the directions given in 42. When finely powdered, 4 parts of the mixed carbonates are sufficient to render the mineral soluble. The following is a description of the method of separating and estimating the alkaline bases, lithia, soda, and potash.

**Separation and Estimation of Alkalies.**—The alkalies present are lithium, sodium, and potassium. They should be converted into sulphates and weighed together, the lithia precipitated as phosphate, and the potassium as the potassio-platinic chloride.

About a gram of the mineral reduced to an impalpable and powder is fused with 10 grams of calcium carbonate and 1.5 gram of ammonium chloride. The substances are intimately mixed, and a layer of the fusion mixture is placed on the top. Fuse for one hour at a good red-heat in a platinum crucible, packed with magnesia inside a Hessian crucible. The contents of the crucible are boiled with water and a little hydrochloric acid, the solution evaporated to dryness, and the silica separated (see p. 200). Filtrate and washings are evaporated to a convenient bulk in a porcelain dish, nitric acid is added to peroxidise the iron, and to the hot solution ammonium chloride and ammonia are added to precipitate iron and alumina. The precipitate is washed and the filtrate mixed with ammonium carbonate and some ammonium oxalate, to precipitate the bulk of the lime as carbonate, and to remove the last traces as oxalate. The liquid is then warmed and allowed to stand for twenty-four hours. The lime salts are filtered off and washed with water containing ammonia. The filtrate should be tested by a further addition of ammonium oxalate, warmed, and allowed to stand for some time. The solution now

contains magnesia and the alkalies, but it is highly charged with ammonium salts; these are destroyed by transferring the liquid to a flask with a round bottom, the neck being supported at an angle of  $45^\circ$ , and boiling with an excess of strong nitric acid until no more effervescence occurs. The liquid may now be evaporated down with strong hydrochloric acid to decompose the nitrates. When brown fumes are no longer disengaged, the chlorides may be evaporated to dryness on a sand-bath, treated with water, and again evaporated until the salts have a neutral or only faintly acid reaction. Barium hydrate dissolved in boiling water is added as long as any precipitate falls; the solution is boiled, filtered, and the precipitate washed with boiling water. The filtrate is tested by a further addition of baryta solution. Boil and add hot dilute sulphuric acid to remove the baryta, the precipitate is allowed to stand for twenty-four hours, the liquid is decanted through a filter (see p. 12), and the precipitate washed with boiling water. Both filtrate and washings are reserved for the estimation of the alkalies.

The foregoing treatment if properly applied has separated all other bases from the alkalies; it is necessary now to evaporate the solution to dryness in a platinum basin; add a little sulphuric acid to expel all other acids, evaporate to dryness cautiously, gently ignite, cool in a desiccator, cover the basin with a film of mica, and weigh the mixed sulphates.

It is necessary to make sure that the alkaline sulphates contain no impurity; therefore dissolve in a small quantity of water and transfer to a beaker; the liquid should be quite free from turbidity. In the event of the liquid not being clear, pass it through a small filter, then add ammonium chloride and ammonium carbonate in small quantity, filter again, evaporate to dryness, and ignite. Weigh as sodium, lithium, and potassium sulphates.

**Estimation of Lithium.**—The sulphates are now dissolved in a small quantity of water, and a few drops of pure caustic soda are added. Calculate now the quantity of disodium orthophosphate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ) necessary to precipitate the lithia, on the assumption that all the salts are lithium sulphate ( $\text{Li}_2\text{SO}_4$ ), and that it will be converted into  $\text{Li}_3\text{PO}_4$ .

Weigh roughly and dissolve the requisite quantity of disodium orthophosphate in water, and add it cautiously, so that no more than is necessary is used to precipitate the lithia from the solution of the sulphates; test whether the solution has an acid reaction, and neutralise or render it slightly alkaline with pure caustic soda. The liquid with the precipitate is now evaporated to dryness, the soluble salts are dissolved out with hot water, and mixed with an equal volume of ammonia solution. Digest on the water-bath, filter after twelve hours, and wash the precipitate with equal volumes of ammonia solution and water. Evaporate the filtrate and first washings to

dryness, and treat the residue as before. If some lithium phosphate is thereby obtained it should be added to the principal quantity. Dry the filter, transfer the pre-precipitate to a porcelain crucible, ignite at a moderate red-heat, and weigh as  $\text{Li}_3\text{PO}_4$ .

Estimations of potash in presence of soda cannot be made with the sulphates or in presence of phosphates. These salts must be converted into chlorides. To the filtrate from the lithia phosphate a hot saturated solution of baryta water, free from alkali, is added as long as a precipitate forms; allow to deposit, filter, wash the precipitate, and pass carbonic acid into the filtrate, to throw down the excess of baryta; heat to boiling, filter off the barium carbonate, wash, add hydrochloric acid to the filtrate, and evaporate to dryness to remove the excess of acid. Effect the separation of the potassium according to the mode of procedure on p. 209.

*Example—*

**Petalite.**—Weight of substance, 1.5684 grams.

**Lithium—**

Weight of platinum basin + cover + mixed	Grams.
sulphates . . . . .	= 86.6595
Weight of platinum basin + cover . . . . .	= 86.4124
<hr/>	
$\text{Li}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$	<u><u>= 0.2471</u></u>

$\text{Li}_3\text{PO}_4$ + crucible + lid	.	.	.	= 17.9270
crucible + lid	.	.	.	= 17.8486

$$\text{Li}_3\text{PO}_4 = \underline{\underline{0.0784}}$$

To find the quantity of lithia,  $\text{Li}_2\text{O}$ , in 1.5684 grams of the mineral—

Parts.	Parts.	
$\text{Li}_3 = 21$	$\text{Li}_2 = 14$	
$\text{P} = 31$	$\text{O} = 16$	$\frac{0.0784 \times 21}{116} = 0.01419 \text{ Li}$
$\text{O}_4 = 64$	—	
—	30	$\frac{0.01419 \times 30}{14} = 0.0304 \text{ Li}_2\text{O}$
<u>116</u>	<u>30</u>	

To find the percentage of lithia  $\text{Li}_2\text{O}$  in the mineral—

$$\frac{0.0304 \times 100}{1.5684} = 1.88 \text{ Li}_2\text{O} \quad \text{Per cent.}$$

**Potassium.**—In this case the potassio-platinic chloride was washed by decantation and transferred by means of a stream of alcohol into a weighed porcelain crucible. The decantations were all passed through a filter.

The alcohol in the crucible is evaporated on the water-bath, and the platinic salt carefully dried in the water-oven. It is then weighed.

	Grams.
$\text{K}_2\text{PtCl}_6$ + crucible + lid	. = 12.6530
crucible + lid	. = 12.4822

$$\text{K}_2\text{PtCl}_6 = \underline{\underline{0.1708}}$$

To find the quantity of potassium in the platinum salt—

Parts.		Gram.
K <sub>2</sub> = 78		
Pt = 197	$\frac{0.1708 \times 78}{488}$	= 0.0273 K
Cl <sub>6</sub> = 213		
<u>488</u>		

The filter through which the solution had been decanted was ignited and weighed in the crucible with the K<sub>2</sub>PtCl<sub>6</sub>. The ignition may be carried out on the lid, the lid afterwards being placed on the crucible.

$$\begin{array}{rcl} \text{K}_2\text{PtCl}_6 + 2\text{KCl} + \text{Pt} + \text{crucible} + \text{lid} & = & 12.6654 \\ \text{crucible} + \text{lid} & = & 12.4822 \end{array}$$

$$\hline 0.1832$$

$$\text{Filter-ash} = 0.0002$$

$$\text{K}_2\text{PtCl}_6 + 2\text{KCl} + \text{Pt} = \underline{\underline{0.1830}}$$

$$\text{K}_2\text{PtCl}_6 + 2\text{KCl} + \text{Pt} \quad . \quad . \quad . = 0.1830$$

$$\text{K}_2\text{PtCl}_6 \quad . \quad . \quad . \quad . = 0.1708$$

$$\hline 2\text{KCl} + \text{Pt} = \underline{\underline{0.0122}}$$

To find the quantity of potassium in the portion of the platinum salt ignited—



Parts.	
$K_2 = 78$	$0.0122 \times 78$
$Cl_2 = 71$	$\frac{\quad}{346} = 0.0275 K$
$Pt = 197$	
<u>      </u>	
346	
<u>      </u>	

Potassium in the platinic salt . . . = 0.0273

Potassium as  $2KCl + Pt$  . . . = 0.0027

Total potassium = 0.0300

To find the percentage of potash  $K_2O$  in the mineral—

Parts.	
$K_2 = 78$	$0.03 \times 94$
$O = 16$	$\frac{\quad}{78} = 0.0361 K_2O$
<u>      </u>	
94	
<u>      </u>	

$$\frac{0.0361 \times 100}{1.5684} = 2.30 K_2O \quad \text{Per cent.}$$

**Sodium.**—The mixed sulphates weigh 0.2471 gram.

$$Li_2O = 0.0304$$

$$K_2O = 0.0361$$

The lithia and potash must be calculated as sulphate and deducted from the mixed salts.

Parts.	Parts.	
Li <sub>2</sub> = 14	K <sub>2</sub> = 78	$\frac{0.0304 \times 110}{30} = 0.1114 \text{ Li}_2\text{SO}_4$
S = 32	S = 32	
O <sub>4</sub> = 64	O <sub>4</sub> = 64	$\frac{0.0361 \times 174}{94} = 0.0668 \text{ K}_2\text{SO}_4$
—	—	
110	174	
<u>      </u>	<u>      </u>	

Mixed sulphates    Li<sub>2</sub>SO<sub>4</sub>    K<sub>2</sub>SO<sub>4</sub>    Na<sub>2</sub>SO<sub>4</sub>

$$0.2471 = 0.1114 + 0.0668 + 0.0689$$

Na <sub>2</sub> = 46	Na <sub>2</sub> = 46	$\frac{0.0689 \times 62}{142} \text{ Grams.}$
S = 32	O = 16	
O <sub>4</sub> = 64	—	$\frac{0.03 \times 100}{1.5684} \text{ Per cent.}$
—	62	
142	<u>      </u>	
<u>      </u>		<u>      </u>

Petalite—	Found. Per cent.
Silica	68.68
Lime	0.79
Magnesia	0.34
Lithia	1.88
Potash	2.30
Soda	1.91
Ferric oxide	0.96
Alumina	23.27
	<u>      </u>
Total	<u>100.13</u>

*Notes.*—(1.) When the alkalies have been obtained as sulphates they are not likely to contain barium, but they may be contaminated by a small quantity of silica, or calcium sulphate. This salt would be sparingly soluble in water at first, and would make the solution turbid. It may be precipitated by the addition of ammonia and ammonium carbonate.

(2.) The reason for the solution becoming acid when lithium phosphate is precipitated may be understood from the following equation :—



Free sulphuric acid, or, what amounts to the same thing in such a solution, acid sodium sulphate is formed.

(3.) By “solution of ammonia” is meant the reagent in common use.

(4.) Lithium orthophosphate is soluble in 2539 parts of pure water, and 3920 of ammoniacal water. When dried at the temperature of 100° C. its composition is represented by  $\text{Li}_3\text{PO}_4$ .

(5.) When lithium phosphate is ignited before being weighed, great care should be taken that the precipitate be removed from the filter before the paper is incinerated.

TABLE OF ATOMIC WEIGHTS BASED UPON THE EXPERIMENTS OF M. STAS, AND CALCULATED BY M. J. D. VAN DER PLAATS (*Ann. de Chimie et de Physique*, 6th series, vol. vii. p. 499, 1886).

		Limit of Accuracy.			Limit of Accuracy.
Aluminium	Al= 27·08	0·05	Molybdenum	Mo= 96	0·3
Antimony	Sb=120	0·2	Nickel	Ni= 58	
Arsenic	As= 75	0·3		or 58·8	0·5
Barium	Ba=137·1	0·1	Niobium	Nb= 94	2·0
Beryllium	Be= 9·1	0·2	Nitrogen	N= 14·05	0·01
Bismuth	Bi=208	0·3	Osmium	Os=195	5·0
Boron	B= 11	0·1	Oxygen	O=16	0
Bromine	Br= 79·955	0·01	Palladium	Pd=106·5	1
Cadmium	Cd=112·1	0·2	Phosphorus	P= 30·95	0·05
Cæsium	Cs=132·8	0·3	Platinum	Pt=194·9	0·2
Calcium	Ca= 40	0·05	Potassium	K= 39·144	0·01
Carbon	C= 12·005	0·005	Rhodium	Rh=104	1·0
Cerium	Ce=141·5	1·0	Rubidium	Rb= 85·4	0·1
Chlorine	Cl= 35·456	0·005	Ruthenium	Ru=104	1·0
Chromium	Cr= 52·3	0·3	Samarium	Sm=150	0·5
Cobalt	Co= 58·8		Scandium	Sc= 44	0·5
	or 60	0·5	Selenium	Se= 79	0·2
Copper	Cu= 63·33	0·02	Silicon	Si= 28	0·1
Didymium	Di=145	3·0	Silver	Ag=107·93	0·01
Erbium	Er=166	2·1	Sodium	Na= 23·05	0·005
Fluorine	F= 19	0·1	Strontium	Sr= 87·5	0·1
Gallium	Ga= 70	1·0	Sulphur	S= 32·06	0·01
Germanium <sup>1</sup>	Gr= 72·28		Tantalum	Ta=182·8	0·5
Gold	Au=196·7	0·5	Tellurium	Te=125	3·0
Hydrogen	H= 1	0·005	Thallium	Tl=204·2	0·5
Indium	In=113·7	0·5	Thorium	Th=233	1·0
Iodine	I=126·86	0·01	Tin	Sn=118·1	0·1
Iridium	Ir=193	0·2	Titanium	Ti= 48·1	0·1
Iron	Fe= 56	0·5	Tungsten	W=184·0	0·2
Lanthanum	La=138	2·0	Uranium	Ur=240	1·0
Lead	Pb=206·91	0·05	Vanadium	V= 51·3	0·1
Lithium	Li= 7·02	0·01	Ytterbium	Yb=173	1·0
Magnesium	Mg= 24·4	0·05	Yttrium	Yt= 89·5	1·0
Manganese	Mn= 55	0·1	Zinc	Zn= 65·3	0·1
Mercury	Hg=200·1	0·2	Zirconium	Zr= 90·5	1·0

<sup>1</sup> Lecocq de Boisbaudran.

## SULPHURIC ACID.

Specific Gravity of Sulphuric Acid at 60° F. or 15° C., calculated from Kolb's Table (Lunge and Hurter).

Degrees Twaddell.	Specific Gravity.	100 parts by weight contain		Grams per litre. H <sub>2</sub> SO <sub>4</sub> .
		SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	
40	1·20	22·10	27·10	325
41	1·205	22·61	27·70	334
42	1·210	23·11	28·31	342
43	1·215	23·60	28·91	351
44	1·220	24·10	29·52	360
45	1·225	24·59	30·13	369
46	1·230	25·09	30·73	378
47	1·235	25·58	31·34	387
48	1·24	26·08	31·95	396
49	1·245	26·57	32·55	405
50	1·25	27·07	33·16	414
51	1·255	27·56	33·77	424
52	1·26	28·06	34·37	433
53	1·265	28·55	34·98	442
54	1·27	29·05	35·59	451
55	1·275	29·54	36·19	461
56	1·28	30·04	36·80	470
57	1·285	30·53	37·41	480
58	1·29	31·03	38·01	490
59	1·295	31·52	38·62	500
60	1·30	32·02	39·23	510
61	1·305	32·51	39·82	520
62	1·31	33·00	40·42	529
63	1·315	33·49	41·01	539
64	1·32	33·97	41·61	549
65	1·325	34·45	42·20	559
66	1·33	34·89	42·73	568
67	1·335	35·32	43·26	577
68	1·34	35·75	43·79	587
69	1·345	36·19	44·32	596

SULPHURIC ACID.—*Continued.*

Specific Gravity of Sulphuric Acid at 60° F. or 15° C., calculated from Kolb's Table (Lunge and Hurter).

Degrees Twaddell.	Specific Gravity.	100 parts by weight contain		Grams per litre. H <sub>2</sub> SO <sub>4</sub> .
		SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	
70	1·35	36·62	44·85	605
71	1·355	37·05	45·38	615
72	1·36	37·48	45·91	624
73	1·365	37·92	46·44	634
74	1·37	38·35	46·97	643
75	1·375	38·78	47·50	653
76	1·38	39·20	48·02	662
77	1·385	39·63	48·54	672
78	1·39	40·05	49·06	682
79	1·395	40·48	49·58	691
80	1·4	40·90	50·10	701
81	1·405	41·33	50·62	711
82	1·41	41·75	51·14	721
83	1·415	42·18	51·66	731
84	1·42	42·60	52·18	741
85	1·425	43·02	52·70	751
86	1·43	43·41	53·18	761
87	1·435	43·81	53·67	770
88	1·44	44·20	54·15	780
89	1·445	44·60	54·64	789
90	1·45	45·00	55·12	799
91	1·455	45·39	55·61	809
92	1·46	45·79	56·09	818
93	1·465	46·18	56·58	828
94	1·47	46·58	57·06	838
95	1·475	46·98	57·55	848
96	1·48	47·34	58·00	858
97	1·485	47·71	58·45	867
98	1·49	48·08	58·90	877
99	1·495	48·44	59·35	887

SULPHURIC ACID.—*Continued.*

Specific Gravity of Sulphuric Acid at 60° F. or 15° C., calculated from Kolb's Table (Lunge and Hurter).

Degrees Twaddell.	Specific Gravity.	100 parts by weight contain		Grams per litre. H <sub>2</sub> SO <sub>4</sub> .
		SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	
100	1·50	48·81	59·80	897
101	1·505	49·18	60·25	907
102	1·51	49·55	60·70	917
103	1·515	49·91	61·15	926
104	1·52	50·28	61·60	936
105	1·525	50·65	62·05	946
106	1·53	51·00	62·50	956
107	1·535	51·36	62·95	966
108	1·54	51·73	63·40	976
109	1·545	52·10	63·85	986
110	1·55	52·46	64·30	996
111	1·555	52·83	64·75	1006
112	1·56	53·20	65·20	1017
113	1·565	53·57	65·65	1027
114	1·57	53·94	66·10	1037
115	1·575	54·33	66·55	1047
116	1·58	54·68	66·98	1058
117	1·585	55·04	67·42	1068
118	1·59	55·39	67·85	1078
119	1·595	55·75	68·29	1089
120	1·6	56·10	68·72	1099
121	1·605	56·46	69·16	1109
122	1·61	56·81	69·59	1120
123	1·615	57·17	70·03	1131
124	1·62	57·52	70·46	1141
125	1·625	57·88	70·90	1151
126	1·63	58·22	71·32	1162
127	1·635	58·56	71·74	1172
128	1·64	58·90	72·16	1183
129	1·645	59·25	72·58	1193

SULPHURIC ACID.—*Continued.*

Specific Gravity of Sulphuric Acid at 60° F. or 15° C., calculated from Kolb's Table (Lunge and Hurter).

Degrees Twaddell.	Specific Gravity.	100 parts by weight contain		Grams per litre. H <sub>2</sub> SO <sub>4</sub> .
		SO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	
130	1·65	59·60	73·00	1204
131	1·655	59·92	73·40	1214
132	1·66	60·25	73·80	1225
133	1·665	60·58	74·20	1236
134	1·67	60·90	74·60	1247
135	1·675	61·23	75·00	1257
136	1·68	61·58	75·43	1268
137	1·685	61·93	75·86	1279
138	1·69	62·28	76·29	1289
139	1·695	62·63	76·72	1300
140	1·7	62·98	77·15	1311
141	1·705	63·33	77·58	1322
142	1·71	63·68	78·01	1333
143	1·715	64·04	78·44	1345
144	1·72	64·39	78·87	1356
145	1·725	64·74	79·30	1367
146	1·73	65·09	79·73	1379
147	1·735	65·44	80·16	1390
148	1·74	65·79	80·59	1402
149	1·745	66·14	81·02	1413
150	1·75	66·49	81·45	1425
151	1·755	66·94	82·00	1438
152	1·76	67·39	82·56	1452
153	1·765	67·84	83·11	1466
154	1·77	68·30	83·67	1480
155	1·775	68·75	84·22	1494
156	1·78	69·20	84·78	1509
157	1·785	69·66	85·33	1523
158	1·79	70·11	85·89	1537
159	1·795	70·56	86·44	1551



SULPHURIC ACID.—*Continued.*

Specific Gravity of Sulphuric Acid at 60° F. or 15° C., calculated from Kolb's Table (Lunge and Hurter).

Degrees Twaddell.	Specific Gravity.	100 parts by weight contain		Grams per litre. $\text{H}_2\text{SO}_4$ .
		$\text{SO}_3$ .	$\text{H}_2\text{SO}_4$ .	
160	1.8	71.02	87.00	1566
161	1.805	71.58	87.69	1582
162	1.81	72.15	88.39	1599
163	1.815	72.71	89.88	1616

Specific Gravities of most highly concentrated Sulphuric Acids at 60° F. or 15° C. (Lunge and Naef).<sup>1</sup>

Tw.	Sp. Gr.	Per cent. $\text{H}_2\text{SO}_4$ .	Tw.	Sp. Gr.	Per cent. $\text{H}_2\text{SO}_4$ .	Tw.	Sp. Gr.	Per cent. $\text{H}_2\text{SO}_4$ .
163.7	1.8185	90	167.4	1.8372	94		1.8412	98
	1.8195	* 90.20		1.8387	* 94.84		1.8406 <sup>2</sup>	* 98.39
164.8	1.8241	91	167.8	1.8390	95		1.8409 <sup>3</sup>	* 98.66
	1.8271	* 91.48		1.8406	* 95.97		1.8403	99
165.9	1.8294	92	168.1	1.8406	96		1.8395	* 99.47
	1.8334	* 92.83		1.8410	* 97		1.8384	* 100.00
166.8	1.8339	93		1.8413	97.70			

<sup>1</sup> *Chem. Industrie*, 1883, February.—The values marked \* are found directly by experiment, the others are interpolated. The weights are reduced to water of 4° C. and the vacuum. All these values refer to *chemically pure acid*. The specific gravity of commercial acids is considerably higher in the case of the highest strengths, but too unequal for acids of different manufactures to admit of embodying them in a table.

<sup>2</sup> Prepared by mixing 95 per cent acid with fuming acid.

<sup>3</sup> Prepared by direct evaporation of 95 per cent acid.

## HYDROCHLORIC ACID.

Percentage of pure HCl grams per litre, 60° F. or 15° C., calculated from Kolb's Results (Lunge and Hurter).

Degrees Twaddell.	Specific Gravity.	Percentage of HCl.	Grams per litre.
1	1·005	1·12	11·32
2	1·01	2·12	21·45
3	1·015	3·12	31·67
4	1·02	4·11	41·99
5	1·025	5·11	52·41
6	1·03	6·11	62·93
7	1·035	7·10	73·55
8	1·04	8·10	84·27
9	1·045	9·10	95·09
10	1·05	10·09	106·01
11	1·055	11·09	117·02
12	1·06	12·09	128·14
13	1·065	13·08	139·36
14	1·07	14·08	150·68
15	1·075	15·08	162·10
16	1·08	16·07	173·62
17	1·085	17·07	185·24
18	1·09	18·07	196·96
19	1·095	19·07	208·78
20	1·10	20·06	220·70
21	1·105	21·06	232·68
22	1·11	22·06	244·80
23	1·115	23·05	257·02
24	1·12	24·05	269·34
25	1·125	25·05	281·76
26	1·13	26·04	294·28
27	1·135	27·04	306·90
28	1·14	28·04	319·62
29	1·145	29·03	332·44
30	1·15	30·03	345·36

HYDROCHLORIC ACID.—*Continued.*

Percentage of pure HCl grams per litre, 60° F. or 15° C., calculated from Kolb's Results (Lunge and Hurter).

Degrees Twaddell.	Specific Gravity.	Percentage of HCl.	Grams per litre.
31	1·155	31·03	358·34
32	1·16	32·02	371·44
33	1·165	33·02	384·64
34	1·17	34·02	397·94
35	1·175	35·01	411·34
36	1·18	36·01	424·84
37	1·185	37·01	438·44
38	1·19	38·01	452·14
39	1·195	39·00	466·00
40	1·20	40·00	479·84

## NITRIC ACID.

SPECIFIC GRAVITY OF NITRIC ACID AT 60° F. (15° C.),  
Calculated from Kolb's Results (Lunge and Hurter).

Degrees Twad- dell.	Sp. Gr.	Percentage by weight.		Grams per litre.	
		HNO <sub>3</sub> .	N <sub>2</sub> O <sub>5</sub> .	HNO <sub>3</sub> .	N <sub>2</sub> O <sub>5</sub> .
1	1·005	·88	·75	8·8	7·5
2	1·01	1·75	1·50	17·6	15·1
3	1·015	2·62	2·25	26·6	22·8
4	1·02	3·50	3·00	35·7	30·6
5	1·025	4·37	3·75	44·8	38·4
6	1·03	5·25	4·50	54·0	46·3
7	1·035	6·12	5·25	63·3	54·2
8	1·04	6·95	5·95	72·3	62·0
9	1·045	7·77	6·66	81·2	69·6
10	1·05	8·59	7·36	90·2	77·3
11	1·055	9·41	8·07	99·3	85·1
12	1·06	10·23	8·77	108·4	97·3
13	1·065	11·06	9·48	117·8	101·0
14	1·07	11·88	10·18	127·1	108·9
15	1·075	12·70	10·89	136·5	117·0
16	1·08	13·52	11·59	146·0	125·1
17	1·085	14·34	12·29	155·6	133·4
18	1·09	15·16	12·99	165·2	141·6
19	1·095	15·98	13·70	175·0	150·0
20	1·100	16·80	14·40	184·8	158·4
21	1·105	17·57	15·06	194·1	166·4
22	1·110	18·35	15·72	203·7	174·6
23	1·115	19·12	16·39	213·2	182·7
24	1·120	19·89	17·05	222·7	190·9
25	1·125	20·67	17·71	232·5	199·3
26	1·120	21·44	18·38	242·3	207·7
27	1·135	22·21	19·04	252·0	216·0
28	1·14	22·98	19·70	262·0	224·6
29	1·145	23·76	20·36	272·0	233·2
30	1·15	24·53	21·03	282·1	241·8

NITRIC ACID.—*Continued.*

SPECIFIC GRAVITY OF NITRIC ACID AT 60° F. (15° C.),  
Calculated from Kolb's Results (Lunge and Hurter).

Degrees Twad- dell.	Sp. Gr.	Percentage by weight.		Grams per litre.	
		HNO <sub>3</sub> .	N <sub>2</sub> O <sub>5</sub> .	HNO <sub>3</sub> .	N <sub>2</sub> O <sub>5</sub> .
31	1·155	25·30	21·69	292·2	250·4
32	1·160	26·08	22·35	302·5	259·3
33	1·165	26·85	23·01	312·8	268·1
34	1·170	27·62	23·68	323·1	276·9
35	1·175	28·40	24·34	333·7	286·0
36	1·180	29·17	25·00	344·2	295·0
37	1·185	29·94	25·66	354·8	304·1
38	1·190	30·71	26·33	365·4	313·2
39	1·195	31·49	26·99	376·3	322·6
40	1·20	32·26	27·65	387·1	331·8
41	1·205	33·02	28·30	397·9	341·1
42	1·210	33·79	28·96	408·8	350·4
43	1·215	34·55	29·61	419·8	359·9
44	1·22	35·32	30·27	430·9	369·3
45	1·225	36·08	30·93	442·0	378·9
46	1·230	36·85	31·58	453·2	388·5
47	1·235	37·61	32·24	464·5	398·1
48	1·240	38·38	32·90	475·9	407·9
49	1·245	39·15	33·55	487·4	417·8
50	1·250	39·91	34·21	498·8	427·6
51	1·255	40·68	34·86	510·5	437·6
52	1·260	41·44	35·52	522·1	447·6
53	1·265	42·21	36·18	532·8	456·6
54	1·27	42·97	36·83	545·7	467·8
55	1·275	43·74	37·49	557·7	478·0
56	1·28	44·50	38·15	569·6	488·2
57	1·285	45·27	38·80	581·7	498·6
58	1·29	46·04	39·46	593·9	509·1
59	1·295	46·80	40·11	606·0	519·5
60	1·30	47·57	40·77	618·4	530·1

NITRIC ACID.—*Continued.*

SPECIFIC GRAVITY OF NITRIC ACID AT 60° F. (15° C.),  
Calculated from Kolb's Results (Lunge and Hurter).

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		HNO <sub>3</sub> .	N <sub>2</sub> O <sub>5</sub> .	HNO <sub>3</sub> .	N <sub>2</sub> O <sub>5</sub> .
61	1·305	48·33	41·43	630·7	540·6
62	1·310	49·10	42·08	643·2	551·3
63	1·315	49·86	42·74	655·6	562·0
64	1·32	50·63	43·40	668·3	572·8
65	1·325	51·40	44·06	681·0	583·8
66	1·33	52·24	44·78	694·8	595·6
67	1·335	53·09	45·51	708·7	607·5
68	1·340	53·94	46·24	722·8	619·6
69	1·345	54·79	46·96	736·9	631·6
70	1·350	55·64	47·69	751·1	643·8
71	1·355	56·53	48·45	766·0	656·6
72	1·36	57·42	49·22	780·9	669·4
73	1·365	58·31	49·98	795·9	682·2
74	1·37	59·21	50·75	811·2	695·3
75	1·375	60·10	51·51	826·4	708·4
76	1·38	61·00	52·29	841·8	721·6
77	1·385	61·97	53·12	858·3	735·8
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88	1·44	74·59	63·94	1074	920·6
89	1·445	75·98	65·13	1097	940·4
90	1·45	77·36	66·31	1122	961·8

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		HNO <sub>3</sub> .	N <sub>2</sub> O <sub>5</sub> .	HNO <sub>3</sub> .	N <sub>2</sub> O <sub>5</sub> .
91	1·455	78·75	67·50	1146	982·4
92	1·46	80·13	68·68	1170	1003
93	1·465	81·52	69·87	1195	1024
94	1·47	82·90	71·05	1219	1045
95	1·475	84·28	72·24	1243	1066
96	1·48	85·66	73·43	1268	1087
97	1·485	87·05	74·61	1293	1108
98	1·49	88·43	75·80	1318	1130
99	1·495	89·82	76·98	1343	1151
100	1·50	91·20	78·18	1368	1173
101	1·505	92·66	79·43	1394	1195
102	1·51	94·13	80·69	1421	1218
103	1·515	95·59	81·94	1448	1241
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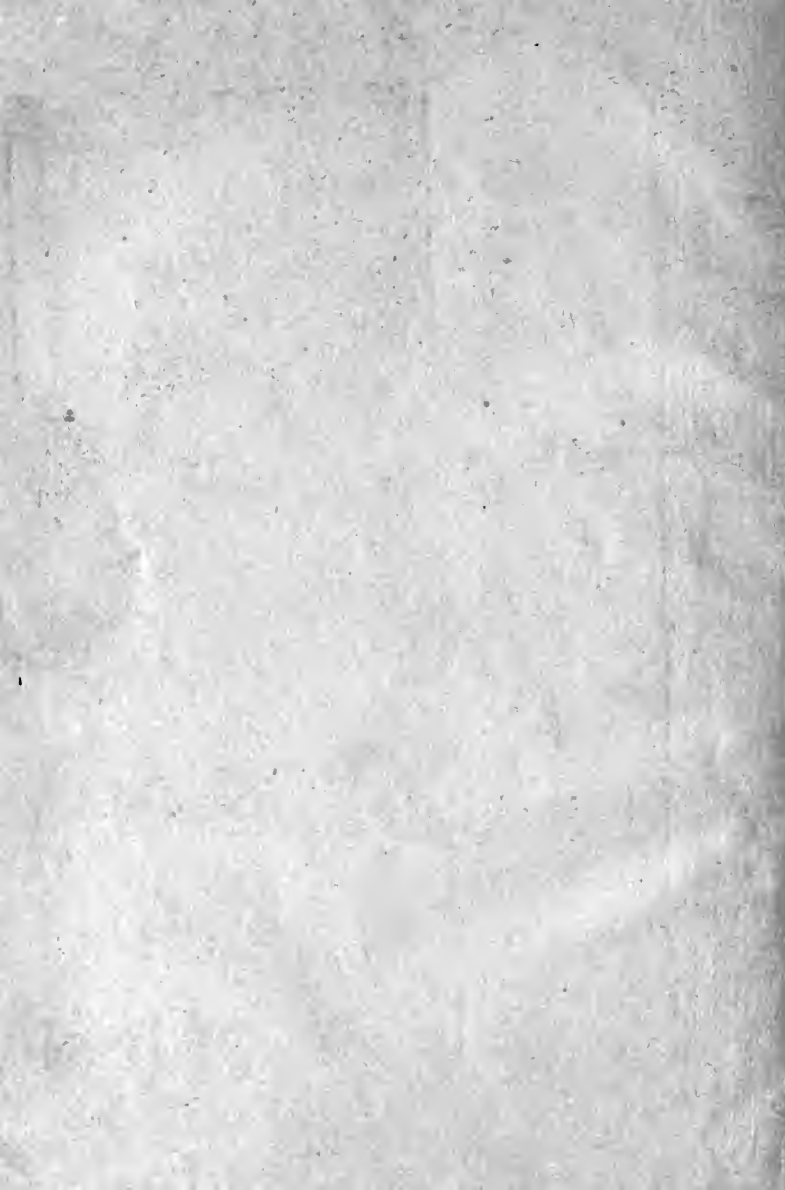
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